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The manual contains a selection of pure chemical substances relevant to waste. By selecting appropriate criteria, it is designed to illustrate part of the danger potential of these substances, at the same time providing pointers as to the possible effects of waste that contains these substances (special-waste). The remarks are complemented by information on the formation and disposal of such waste.

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HAZARDOUS SUBSTANCES IN SPECIAL-WASTES

MANUAL

revised in accordance with the
draft "Manual of Hazardous Waste"
of the Stanford Research Institute
(Menlo Park, California, USA)

prepared on behalf
of the
Federal Ministry of Interior

by the
FEDERAL ENVIRONMENTAL AGENCY
(Berlin-West)
Waste Management Division

October 1976

Committee on the Challenges of Modern Society
North Atlantic Treaty Organisation

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Preface

In the framework of the NATO-CCMS pilot study "Disposal of Hazardous Wastes" the pilot country Federal Republic of Germany offered to submit a first version of a manual "Hazardous Substances in Special-Wastes" as a separate contribution. This proposal was accepted by the Pilot Study Group at a joint session in Bonn in May 1976, and it is the English translation of this manual which is presented here.

The manual originates from a work of the Stanford Research Institute commissioned and financed by the Federal Minister of Interior in 1973/74. Taking into account various national and international efforts in the field of hazardous waste the Federal Environmental Agency (Berlin-West) has revised the draft prepared by the Stanford Research Institute and brought it into line with German conditions.

The manual "Hazardous Substances in Special-Wastes" contains a selection of pure chemical substances relevant to waste. By selecting appropriate criteria, it is designed to illustrate part of the danger potential of these substances, at the same time providing pointers as to the possible effects of waste that contains these substances (special-waste). The remarks are complemented by information on the formation and disposal of such waste.

The manual is thus aimed primarily at those involved with the problem of special-waste within waste management. It is, however, also of significance as a source of data for the field of "environmental chemicals and biocides".

The present edition is only a first start and is designed primarily to illustrate the overall conception of a more extensive and detailed manual to be prepared in the next years; it does not claim to be complete. This applies in particular to the number of substances selected. The reader is, therefore, emphatically recommended to read the following section entitled "Introduction and Explanations". This section also provides a general view of further chapters still being planned and which, together with other substances, are to be included in the manual as it is continued and updated.

Wolbeck

Dr. Wolbeck

Pilot Study Leader

II. INTRODUCTION AND EXPLANATIONS

1. Introduction

1.1 Who is this manual intended for?

The persons addressed by this manual can be broken down into four target groups:

- scientific establishments
- government and administration
- industry and commerce
- general public.

The manual is aimed, on the one hand, at scientific establishments dealing with "environmental chemicals" and problems involved in waste management. On the other hand, it is aimed at persons and establishments at all levels throughout the country engaged in legislation, implementation or jurisdiction in the field of waste management. In this respect, it should be an aid in particular to all those having to attend to waste disposal, such as central, regional and local authorities, when carrying out their work.

The manual is also aimed, however, at industrial plants and trading firms confronted with special-waste and haulage contractors conveying such waste. The circle of users addressed includes above all employees of the companies in question charged with environmental protection.

Last but not least, the manual is also aimed at the general public interested in such issues and which can use the manual as a source or information when, for instance, press reports on toxic waste affairs are to be interpreted or the significance of legal proposals on the monitoring and disposal of special-waste is to be made out.

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The manual is of a chiefly scientific character. It constitutes a first attempt to illustrate the problems involved in special-waste by describing the hazardous substances that it contains.

With such an extensive target group, not all problems involved in special-waste can, of course, be treated and exhausted in this manual. Experts already familiar with the problems at issue may deplore the absence of many a detail. It was, however, intended to provide a clear and straightforward presentation of those characteristics of hazardous substances that are relevant to waste in order to illustrate the total hazard potential of this category of waste.

1.2 What is special-waste?

The Waste Disposal Act of 7 June 1972 does not contain any definition whatsoever of special-waste. With the exception of several wastes governed by special laws, the legislator has only differentiated between waste that can be disposed of together with household refuse and waste that, by its very nature or quantity, cannot be disposed of together with household waste. The term "special waste" has become established for the latter case and includes

- waste not subject to the provisions of the Waste Disposal Act (e.g. animal carcasses, used oils, radioactive materials, waste water);
- waste from intensive mass animal breeding;
- offals and waste from meat processing;
- waste from hospitals, doctors' practices and other medical facilities;
- car wrecks;
- used tyres;
- other waste specific to production and utilization,

special-waste above all being understood, strictly speaking, as waste from the latter group.

In particular, such waste stems, for instance, from the

- chemical industry
- pharmaceutical industry
- metal working industry
- glass working industry
- oil refining industry
- plastics, rubber and asbestos processing industries
- textile industry
- leather fabrication
- wood, paper and printing industries.

Special-waste is characterized on the basis of its special nature by the properties of the pollutants contained in it. Some of these properties are, for example, as follows:

- Toxicity
- Hazards to health
- Hazards to water
- Danger of infection
- Danger of explosion
- Danger of fire
- Danger of corrosion.

The properties of special-waste must also be considered when being defined. Discussions centring on an official definition of this term are still under way as the term toxicity continues to be controversial on the one hand, and on the other it has not so far been possible to find any criteria for the selection of toxic substances to be treated. By way of example, two definitions are listed below illustrating the problem. The Commission of the European Communities proposes the following definition for a guideline on the disposal of toxic and hazardous wastes:

"Toxic or hazardous wastes as provided for by this guideline are substances, products or sub-products stemming from industrial, commercial, handicraft, agricultural or scientific activities and the derivation or depositing of which constitutes a direct or long-term risk for man and the environment on account of their toxic properties, stability or concentration and must therefore be subjected to particular controls, and for which priority methods of treatment and disposal are to be recommended."

This definition is essentially of a practical nature, while at the same time a definition in its own right.

The following definition of a specific term for waste as covered by "special-waste" is to be added to the amendment to the Waste Disposal Act as a new paragraph 2 of § 2:

"Additional requirements are to be made in accordance with the present Act on the disposal of waste from industrial or other business enterprises which, in terms of nature, condition or quantity, is particularly hazardous to health, air or water, is explosive or combustible, or contains or can cause vectors of contagious diseases. Waste as defined in sentence 1 is designated by the Federal Government by virtue of an order with the approval of the Bundesrat (Federal Council)."

The principal task involved in such a definition will be to draw up a concrete list of corresponding wastes on the basis of the criteria specified.

1.3 How is special waste brought under control and how is it treated?

There are legal, institutional and technical possibilities - which have to complement each other - of keeping environmental disorders possibly originating in special waste as small as possible. The following are priority measures in the disposal of special waste:

- Improvement of existing laws and orders with regard to complete control of the waste from the producer to the transporter and on to the disposal expert
- Providing owners of wastewith better information about suitable possibilities of disposal
- Rapid preparation of individual waste disposal plans for special waste
- Introduction of a duty to report and certify plants and systems in which special waste is produced
- Appointment of a works employee responsible for waste
- Checking of requirements to be met by the transportation of waste
- Construction and expansion of disposal facilities for special waste.

The technical possibilities consist above all in the creation of efficient, supra-regional central facilities for the treatment, disposal and recycling of special waste.

Efforts can be made to organize such facilities both on a private enterprise basis and in the form of joint solutions between the representatives of public interests and the business sector as, for instance, already practised in Bavaria, Hesse and Baden-Württemberg.

The technical equipment of facilities for treating toxic wastes is broken down into the following groups:

- Temporary storage (container storage areas, warehouses, e.g. for cyanide hardening salts)
- Pre-treatment systems (e.g. detoxication, neutralization, dewatering, decanting, emulsion separation)
- Special dump for solid and compact wastes chiefly of an inorganic nature (occasionally also with special containers for temporary storage of liquid and sludgy waste)
- Special incinerator for special waste of liquid or pasty consistency (chiefly organic waste) with absorptive or adsorptive gas purification
- Facilities for recycling certain wastes or their valuable contents (e.g. solvent distillation, metal extraction from electroplating sludges)

Efforts will generally be made to pool all such groups of facilities in one location. Wherever, for instance, the hydrogeological situation does not permit the establishment of a dump for special waste at the same location, a group of facilities can also be set up away from the latter. To economize transportation costs, it has proven advantageous to assign collection centres to the central disposal facilities for the purposes of local collection, temporary storage and partial pretreatment of the waste delivered.

The cost of disposing of special waste fluctuates within wide limits on account of the large number of methods and processes applied. The charges for substances that can be dumped without pre-treatment range from 30 to 50 German Marks per ton, while the price for special waste requiring chemical or thermal treatment may rocket into the several hundreds of Marks.

Reference should also be made in this connection to two types of special waste which give rise to particular problems and for which supra-regional, nation-wide disposal provisions are available:

- Cyanide hardening salts are at present properly stored in a central location for the entire Federal Republic of Germany in a disused rock salt mine in Herfa-Neurode/Hesse.
- Large quantities of chlorinated hydrocarbons are burned on special ships on the high seas.

The addresses of enterprises involved in the disposal of special waste are listed in Section IV of the manual.

1.4 Which aspects of special waste are dealt with in this manual?

Anyone reading this manual for the first time will very soon ask to what extent its title is in line with the contents. This is, however, primarily a list of individual hazardous substances, and not a selection and characterization of special waste. This conception provides for a presentation of hazardous chemicals within flows of waste and not the flows of waste themselves as their varying material composition means that they are difficult to define in practice. The advantage of this procedure is that essential data and information about substances and groups of substances can be combined in the form of data sheets.

When characterizing special waste, a whole series of material properties is to be borne in mind, toxicity being at the top of the list. Most of the substances relevant to waste and described in the manual were selected on the basis of their toxicity, and not on the basis of other hazardous properties. Treatment of radioactive and infectious waste would at any rate be going beyond the present scope of this manual.

The data sheets tabulate physical, toxicological and otherdata relevant to the environment, and contain a textual section pointing out hazards to the environment, in addition to the formation and treatment of waste. Technical details as to the origin and treatment of special waste were only presented insofar as they are of importance for the decision as to how the waste in question is best conveyed for proper treatment, disposal or recycling. In view of this objective, the manual is based more on secondary literature and appropriate summaries rather than on research-oriented primary literature.

When drawing up this manual, the authors frequently had to take decisions and make assessments as to which substances and data should be considered in an initial draft. Consequently the manual, in its present version, contains only 90 individual substances, which are to be increased to approx. 400 within the scope of continuation and updating. This is a modest number in comparison to all the hazardous chemicals. Of the huge number of hazardous substances, it was, however, attempted to place the emphasis above all on the most significant in terms of waste management.

When interpreting the toxicity data, it should be borne in mind that virtually all existing data relating to toxicity are based on tests with pure compounds and cannot, therefore, be unquestioningly applied to all waste.

The manual "Hazardous Substances in Special Waste" does not and cannot represent complete treatment of all aspects of this group of substances. It should rather be understood as a framework for discussion, providing an impetus for further investigations and potential solutions so as to guarantee due and proper treatment and disposal of special waste.

1.5 What is planned?

The scope of the present draft manual had to remain restricted in view of the time and means available. It is, however, intended to continue the book (loose-leaf collection) and at the same time provide consideration of the following points (cf. also chart):

- Supplementation of the data section by additional hazardous pure substances
- Supplementation of the data in the cover sheet in line with the latest state of knowledge (for example, many boxes in the safety guideline section had to remain blank because the corresponding orders and guidelines still contain too little information)
- Conversion to international SI units
- Supplementation of the list of German plants for the treatment of special waste
- Inclusion of a list of German research institutes chiefly preoccupied with the problem of special waste
- Improvement in the sections on the formation and treatment of waste after the provision of a library - still to be set up by the Federal Environmental Agency - covering processes involved in production techniques and sources of waste
- Elaboration of a list of flows of waste within certain branches of industry, such a list being in line with German conditions
- Inclusion of safety guidelines governing the handling of special waste

Manual "Hazardous Substances in Special Waste"

Preface

Introduction
Explanations

Data sheets

Library covering processes involved

Index of flows of waste

Legal bases

List of facilities

Research institutes

Glossary

Group index
Substance index

General literature

Manual "Hazardous Substances in Special Waste"	Manual "Hazardous Substances in Special Waste"
Preface	Preface
Introduction	Introduction
Explanation	Explanations
General literature	
Data sheets	Data sheets
	Library covering processes involved
	Index of flows of waste
	Legal bases
List of facilities	List of facilities
	Research institutes
Glossary	Glossary
Group index Substance index	Group index Substance index
	General literature
as per 1975	as per 1977/78

Its internal ordering and arrangement and the projected issuing of supplementary editions mean that the manual can be extended and supplemented at all times. Above all the experiences and comments of the users are to be considered when the manual is continued. The present preliminary edition could not be prepared in the form of a loose-leaf collection for cost reasons.

2. Explanations

2.1 Breakdown of Sections (present form)

The manual is broken down into two sections dealing with the substances (III, VII) and five subsidiary sections (I, II, IV, V, VI).

The section dealing with the substances contains a list of data sheets for hazardous substances or groups of hazardous substances. At the beginning of a data sheet (cover sheet) there is tabulated information as to the properties of the substance dealt with. Particular emphasis was attached to stating the range of toxic concentrations for the essential groups of organisms and providing limits for water and air from the relevant safety guidelines of the Federal Republic of Germany, European Communities and the USA. In the following textual section there is first a description of the substance or material and then a closer look is taken separately at hazards to man, hazards to the environment, production and use of the substances, formation of the waste and possibilities of its treatment. There is a cover sheet for almost every substance described in the textual section.

Deviations were occasionally made from the abovementioned sequence of individual topics in the textual section for large classes of substances, in particular metals and metal compounds, for reasons of clarity.

The substances or groups of substances are not arranged alphabetically. Instead, it was attempted, following efforts undertaken in the European Community, to break down toxic waste into individual major groups. They were broken down in the manual in such a way that

- all toxic wastes or environmental chemicals are covered by the list of major groups
- the sequence of listing does not permit any order of priority of the individual substances with regard to the severity of the hazards they present to the environment.

The latter point is of importance because the authors feel that although there can be more or less toxic pure substances, it cannot necessarily be concluded that there is waste containing these substances that is more or less toxic on account of its different composition.

Each major group was assigned a letter; each individual compound to be classified in it was given a number. Alphabetical ordering was dispensed with in view of the manual being continued and extended by additional individual substances.

A list of major groups and alphabetical index can be found in Section VII. The list of major groups is for classification purposes only; it is not meant to be used to locate certain substances. For this purpose the alphabetical index is always to be consulted.

The subsidiary sections in the manual are broken down into the Preface (I), Introduction and Explanations (II), a list of all facilities for the disposal of special waste in Germany (IV) and a glossary with selected explanations of terms or the technical words used in this manual (V). The manual is rounded off by a general survey of literature (VII) supplementing the special literature at the end of each data sheet.

2.2 Notes on the Data Section

The items numbered on the following sample cover sheet are explained below:

(1) Data sheet number

The system can be seen from the classification of hazardous wastes into 15 major groups (see p. 16) given in Section VII.

(2) Name of substance or group of substances

For individual substances the scientific name or common designation has been given. For substances belonging to a class of compounds for which there are a number of data sheets, the name of the class of compounds has been given.

(3) Name of substance

The name given here designates exactly the compound referred to in the data section of the data sheet.

(4) Empirical formula (molecular formula)

Gives in chemical symbols the number and kind of atoms in a molecule of the compound concerned.

(5) Simplified structural formula

Indicates in greater detail the arrangement of certain groups of atoms in the compound described.

A Organohalogen compounds
B Organic sulphur, nitrogen, nitro and phosphorus compounds, excluding biocides
C Isocyanates
D Nitriles
E Cyanides and substances which can form cyanides
F Polycyclic hydrocarbons, including condensed systems
G Phenols and their derivatives
H Solvents without organohalogen compounds
I Biocides, pharmaceuticals and compounds derived from them, including pesticides
K Tars and tar-like products
L Organic and inorganic acids, bases and anhydrides
M Metals, metallic compounds or metal-containing inorganic or organic compounds of the following metals
N Aldehydes
O Potentially unstable substances (explosive, strongly oxidizing, polymerizing etc.)
P Miscellaneous

(1)

(2)

(3)

Formula (4) (5) **CAS no.** (6)

Synonyms (7)

Appearance (8)

Melting point (9)

Boiling point (10)

Vapour pressure (11)

Density (12)

Vapour density ratio (air = 1) (13)

Solubility in water (14)

Flash point (15)

Ignition temperature (16)

Inflammable mixture (17)

Toxicity range for short-term exposure: (18)

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols (19)

Safety guidelines (20)

Air **mg/m^3**	MAK	TLV	MIK (20c)		TA Luft (20d)			
	(20a)	(20b)	1/2 h	24h	IW_1	IW_2	KL_S	KL_G

Water **mg/l**	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
	(20e)	(20f)	A_1	A_2 (20g)	A_3	(20h)

Remarks (21)

(6) CAS no.

In addition to the usual chemical identification with name, synonym and formulas, the identification numbers of the Chemical Abstracts Service (CAS) have been listed for most chemicals. This is an identification number that is used virtually in all international identification systems and provides access to additional sources of data and literature.

(7) Synonyms

For many of the names given in item (3) there are several common designations. The most important ones have been noted and are also contained in the alphabetical index.

(8) Appearance

Telegraphic information on the physical state, colour, odour and other conspicuous properties of the substances.

(9) Melting point

Denotes the temperature in °C at which a substance under standard pressure (760 torr) changes from the solid to the liquid state.

(10) Boiling point

Denotes the temperature in °C at which a liquid under standard atmospheric pressure (760 torr) changes from the liquid to the gaseous state.

(11) Vapour pressure

Denotes the pressure in torr (= mm Hg) at 20°C which a vapour in a closed container and in equilibrium with its solid or liquid form exerts on the enclosing walls.

(12) Density

Denotes the mass in g contained in one cm^3 of a substance at 20°C and 760 torr.

(13) Vapour density ratio

Relative to air = 1, this quantity denotes how many times heavier or lighter a substance is in comparison to the same amount of air. Values greater than 1 mean that the vapour or the gas sinks in air; values below 1 indicate that it rises.

(14) Solubility in water

Denotes the maximum amount of the substance concerned that dissolves in water at a certain temperature. This solution is then called concentrated or saturated.
For reasons of clarity and practicability, the solubility has been given primarily in words, as explained below:

very highly soluble = soluble in less than 1 part solvent
highly soluble = soluble in 1 - 10 parts solvent
soluble = soluble in 10 - 100 parts solvent
slightly soluble = soluble in 100 - 1000 parts solvent
very slightly soluble = soluble in 1000 - 10000 parts solvent
virtually insoluble = soluble in more than 10000 parts solvent

(15) Flash point

Denotes the lowest temperature in ^{o}C at which vapours are given off in such quantities from a liquid under a pressure of 760 torr that they form an inflammable mixture with the air above the liquid.

(16) Ignition temperature

Denotes the temperature in ^{o}C, under defined experimental conditions, at which a gas-air or vapour-air mixture having good ignition qualities will just burn with a flame when brought in contact with a wall heated to this temperature.

(17) Inflammable mixture

Denotes the concentration range (in vol.%) of a vapour or gas in a mixture with air at which the inflammable or explosive mixture will ignite and continue burning on its own after ignition.

(18) Toxicity range for short-term exposure

Most of the data listed were taken from the condensed version of a literature and data compilation prepared by the HYGIENE-INSTITUT DES RUHRGEBIETS, GELSENKIRCHEN ("Gelsenkirchner Dokumentation").
The authors felt this study to be the most suitable data compilation, for the purpose intended, in the field of effective concentrations of harmful or toxic substances in water for various groups of organisms in the event of oral intake or contact with the water.

The data for the various groups of organisms denote the range (range = scatter of the literature values) in which the material being considered produces toxic or harmful effects as the result of a short-term exposure (acute action). The concentration data for man and warm-blooded animals are given in mg or g/kg, that is relative to the weight of the test subject. The data for fish and lower water organisms are given in mg/l and refer to water.

In the textual section of a data sheet, other literature sources are also often quoted under the item "Hazards to the Environment" in addition to the data in the data sheet. The following terms appear often in this connection:

Danger threshold

Denotes the concentration of a toxic substance at which no injuries in the form of symptoms have occurred after an exposure (fish in most cases) of approx. 1 hour.

Toxic concentration limit

Denotes the concentration upon the exceeding of which the start of toxic action can be established.

LD or LC (Lethal Dose or Lethal Concentration)

Denotes a fatal concentration for fish and other water organisms. The value is usually accompanied by an index indicating in % the number of organisms killed: e.g. LD_{50} (median lethal dose) denotes the concentration of a toxic substance at which 50% of the organisms have been killed after a defined time.

TLm Median tolerance limit. A common synonym in English-speaking countries for LD_{50} or LC_{50}.

(19) Occupanional safety - Danger symbols

These danger symbols have been taken from the Occupational Safety Act, dated 17 September 1971 (Bundesgesetzblatt (BGBl)/Federal Law Gazette No. 100, 1971, p. 1601), covering hazardous substances. The meanings are as follows:

E = explosion hazard
O = conducive to fire
F = easily inflammable
T = toxic
C = corrosive
Xn = hazardous to health
Xi = irritant.

(20) Safety guidelines

Compilation of the most important laws, acts and guidelines containing relevant data on hazardous substances in air or water. As appropriate values are not yet available in Germany for many substances, data have been taken also from the Anglo-American sector. This provides at least some idea of the order of magnitude of certain limits.

(20a) MAK values

Maximum workplace concentrations
Literature: report X, dated 14 June 1974, of the Commission for Testing Materials Hazardous to Health (German Society for the Advancement of Scientific Research, Bonn/Bad Godesberg).
The MAK values are a measure of the concentrations of a certain hazardous substance that can just be tolerated when working with this substance for approx. eight hours. These values are recommended and not legally binding.

(20b) TLV

Threshold limit values
Data from the Anglo-American sector comparable to the German MAK values. The data listed have been taken from the American draft of the manual (see literature).

(20c) MIK

Maximum immission concentrations for an exposure of 1/2 hour and of 24 hours (mean values). Designates maximum concentrations of air-polluting substances in air layers close to the ground generally recognized as safe for man, animals and plants on the basis of present experience. These are values recommended by the VDI (Verein Deutscher Ingenieure/Society of German Engineers) and have been published in the VDI Richtlinien (VDI Guidelines) No. 2310 and 2306.

(20d) TA Luft

Manual, dated 28 October 1974, giving instructions on how to keep the air clean. First set of general administrative regulations for the German Federal Immissions Law (Bundes-Immissionsschutzgesetz) (Gemeinsames Ministerialblatt (GMBl.)/Common Ministerial Gazette 1974, 24, p. 426).

The meanings are as follows:

IW_1 (IW1) = Immission value for long-term exposure to gases

IW_2 (IW2) = Immission value for short-term exposure to gases

Kl_S = Classification of certain dust-like emissions in waste gas

Substances of Class I (for a mass flow of 0.1 kg/h and more)	20 mg/m^3
Substances of Class II (for a mass flow of 1 kg/h and more)	50 mg/m^3
Substances of Class III (for a mass flow of 3 kg/h and more)	75 mg/m^3

Kl_G = Classification of vapourous or gaseous emissions of organic compounds in waste gas

Organic compounds of Class I (for a mass flow of 0.1 kg/h and more) : 20 mg/m^3

Organic compounds of Class II (for a mass flow of 3 kg/h and more) :150 mg/m^3

Organic compounds of Class III (for a mass flow of 6 kg/h and more) :300 mg/m^3

(20e) TwVO (also TVO)

Limit values for chemical substances as provided for by the act covering drinking water and process water for food-processing plants (Trinkwasserverordnung/Drinking Water Act) dated 31 January 1975 (BGBl. 1975, No. 16, p. 453).

(20f) PLWS

Provisional limits in water and soil
Limit values suggested by the TRW Systems Group (see literature under II.3.) for substances endangering water and soil. The values are only of a guideline nature.

(20g) ENV. 140 (EEC)

EEC document ENV 140 on the guideline covering quality requirements to be met by surface water used to provide drinking water.
The meanings are as follows: A1, A2, A3 = water of the required quality to provide drinking water for human consumption after simple (A1), conventional (A2) or thorough (A3) physical and chemical treatment and sterilization.

(20h) VLwF Group

Group designation from the list of water-endangering substances given in the act governing the storage of water-endangering liquids dated 19 April 1968 (North Rhine-Westphalia).

The meanings are as follows:

S = Substances which, as a rule, are water-endangering even in small amounts

M = Substances which, as a rule, are water-endangering only in larger amounts

L = Substances which, as a rule, are water-endangering only in very large amounts.

(21) Remarks

This space is used for brief information on conspicuous features or properties not described in greater detail. Wherever required, the conversion from mg/m^3 into ppm has been given.

Finally, it should also be pointed out that because of the wide spectrum of users and associated requirement of practicabilitythe current units of measure have still been used in the present draft. Within the scope of continuation, however, the changeover to international SI units shall have been effected by 1977.

DATA SHEETS

A ORGANOHALOGEN COMPOUNDS

A 1	Epichloroohydrin
A 2	Trichloroethane
A 3	Dichloroethane
A 4	Dibromoethane
A 5	Ethylene Chlorohydrin
A 6	Allyl Chloride
A 7	Methyl Chloride
A 8	Carbon Tetrachloride
A 9	Chloroprene
A10	Dichlorodiisopropyl Ether
A11	1,2-Dichloropropane
A12	
A13	
A14	
A15	
A16	
A17	
A18	
A19	
A20	

Epichlorohydrin

EPICHLOROHYDRIN

Formula C_3H_5ClO $CH_2(O)CHCH_2Cl$ **CAS no.** 106898

Synonyms 1-chloro-2,3-epoxypropane, 1-epichlorohydrin
1-chloropropylene oxide, chloromethyloxirane

Appearance colourless liquid, chloroformlike odour

Melting point	-48°C
Boiling point	116.5°C
Vapour pressure	17 torr at -4°C
Density	1.18 g/cm^3
Vapour density ratio (air = 1)	3.29
Solubility in water	very slightly soluble
Flash point	34°C
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	90 - 238 mg/kg
Fish	1 - 100 mg/l
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	18	19						I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
		0.95				

Remarks Danger of resorption through the skin

1 mg/m^3 ≙ 0.245 ppm
1 ppm ≙ 4.1 mg/m^3

EPICHLOROHYDRIN

Description of Material

Epichlorohydrin is a colourless, highly fluid liquid of chloroformlike odour. The reactivity of the compound is characterized by the terminal chlorine atom and the epoxy group. Other groups may be added easily by exchange reactions, so that the substance may be used in many different ways in the synthesis of glycerol and epoxy resins, for example.

Hazards to Man

Epichlorohydrin causes strong local irritation and severe corrosion of skin tissue, mucous membranes and particularly the eyes (formation of vesicles). Also, it is resorbed through the intact skin in the form of vapours. Accompanying an acute poisoning are - frequently delayed - nausea, respiratory depression or respiratory paralysis. Chronic damage has been observed in inflammatory changes of the eyes and lungs as well as kidney and liver damage (fatty liver). Sensitive persons tend to develop allergies. In order to prevent injuries protective clothing (breathing protection) should be worn on the job. The olfactory threshold of 10 ppm is so high that injuries to health had occurred usually before the odour had been detected. After an accident all contaminated clothing has to be changed and the skin carefully cleaned with water.

With air, epichlorohydrin vapours form explosive mixtures, the ignition of which is possible at hot surfaces, by sparks and open flames. Highly poisonous and aggressive gases (hydrogen chloride, phosgene) are liberated during burning. Acids, caustic solutions and halide salts initiate polymerization reactions.

Violent reactions take place with alcohol-containing materials.

In combination with moisture, steel is attacked, a fact which has to be considered in selecting storage tanks. Generally, storage areas should be cool, dry and well ventilated (danger of fire!).

Hazards to the Environment

The poisonous action on plankton, fish and mammals has been demonstrated. The poisonous concentration for fish lies in the range of 1-100 mg/l (Lit.1). The LD_{50} values for rats, guinea pigs and rabbits are reported to be 141, 195, 280 and 345 mg/kg (Lit.1). On the basis of these values, epichlorohydrin is classified as a highly poisonous substance.

Production and Use / Waste Formation

Epichlorohydrin is prepared in technical quantities from propylene by the Bertholet method. In this method propylene is converted to allyl chloride by means of gaseous chlorine at 500°C, which in turn forms glycerol dichlorohydrin through addition of hypochloric acid. Upon hydrolysis with calcium hydroxide, epichlorohydrin evolves.

Epichlorohydrin is used for the synthesis of glycerol. It is further an intermediate product for many organic syntheses and starting material for the production of epoxy and phenolic resins. It serves as a solvent for impregnating resins (paper finishing), for vulcanization of propylene-based rubber, and in the processing of cellulose esters and ethers. It is used as a stabilizing agent for insecticides and a soil-disinfecting compound.

During the mentioned production and processing procedures waste materials are obtained which always contain, besides epichlorohydrin, other dangerous substances. The largest quantities of epichlorohydrin containing wastes originate in the production of epoxy and phenolic resins (Lit.2).

EPICHLOROHYDRIN

Waste Treatment

Aqueous, epichlorohydrin-containing wastes are saponified by caustic solutions and the resulting glycerol is biodegraded in sewage treatment plants (Lit.3). It is expedient to destroy concentrated wastes in special incinerators in order to avoid the formation and emission of phosgene due to improper incineration (Lit.2). Larger quantities of these wastes have to be burnt at high sea.

Literature

1) "Evaluation of the Hazard of Bulk Water Transportation of Industrial Chemicals, A Tentative Guide", National Academy of Sciences 1970

2) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste, issued for the EPA, TRW Systems Group, PB 224579, Set/AS, 1 February 1973

3) "Treatment of Wastewater from the Production of Polyhydric Organics", Water Pollution Control Research Series, 12020EEQ 10/77, issued for the EPA by Dow Chemical Company. Freeport, Texas: October 1971

1,1,1-Trichloroethane

TRICHLOROETHANE

Formula	$C_2H_3Cl_3$	CH_3CCl_3	**CAS no. 71556**

Synonyms methylchloroform, chlorothene stabilized

Appearance colourless liquid with chloroformlike odour

Melting point	-32°C
Boiling point	74.1°C
Vapour pressure	100 torr at 20°C
Density	1.31 g/cm^3
Vapour density ratio (air = 1)	4.55
Solubility in water	very slightly soluble (0.05 wt %)
Flash point	not readily flammable+)
Ignition temperature	537°C
Inflammable mixture	8.0 - 15.5 vol.°/o

Toxicity range for short-term exposure:

Man	0.5 - 5 g/kg
Warm-blooded animals	0.75 - 14.3 g/kg
Fish	75 - 100 mg/l
Lower water organisms	

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
	1080	1900	90	30				III

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A$_1$	A$_2$	A$_3$	
		19				

Remarks

+) Danger of ignition or explosion by sparks or open flame with high

1 mg/m^3 $\hat{=}$ 0.180 ppm

1 ppm $\hat{=}$ 5.545 mg/m^3

Description of Material

1,1,1-Trichloroethane is a colourless liquid of chloroformlike odour and is very slightly soluble in water. Commercial trichloroethane contains inhibitors (stabilizers) in order to prevent the attack of various materials (e.g. aluminium) due to slow decomposition.

Hazards to Man

1,1,1-Trichloroethane affects the central nervous system in a similar manner (somewhat weaker) as chloroform or trichloroethylene. In high concentrations the effect corresponds to that of typical narcotics. The concentration for a deep narcosis is about 5000 ppm (Lit.1). Lethal concentrations paralyze the control centres for breathing and/or circulation. Compared to the other narcotics the circulation-inhibiting action of 1,1,1-trichloroethane is noticeably stronger (Lit.2).

Liquid 1,1,1-trichloroethane acts as a defatting agent on the outer skin and has a slight irritating effect there (Lit.3,4). Higher concentrations irritate the mucous membranes of the respiratory system (Lit.3-6). Resorption through the intact skin is low (Lit.7).

Absorbed 1,1,1-trichloroethane is exhaled for the most part in unchanged form through the lungs. The biological half-life is 4 hours for man (Lit.8). Exposure to narcotic concentrations over several hours may, however, lead to liver and kidney damage (Lit.9,10,11).

Heating or ignition of 1,1,1-trichloroethane results in the formation of phosgene, chlorine and in particular hydrogen chloride.

Hazards to the Environment

In spite of its low solubility in water (about 0.05 weight per cent), 1,1,1-trichloroethane can, if introduced into water, become a hazard to water organisms. One indication of this is the lethal dose of 75-100 mg/l (Lit.12) determined for a certain species of perch. In general, the lethal concentration to fish is considered to be between 150 and 175 mg/l (Lit.13). 1,1,1-Trichloroethane is therefore a water-endangering liquid according to the "storage container regulations" (VLWF).

Production and Use/Waste Formation

In order to prevent the formation of an inordinate amount of undesired isomers (e.g. the 1,1,2-compound), the synthesis of 1,1,1-trichloroethane is normally carried out step by step. Several processes of oxychlorination technology compete. Vinyl chloride is the starting material for one of these processes. Another process starts from 1,1-dichloroethane (ethylidene chloride), which is chlorinated in the presence of a stabilizer. The chlorinated product is cracked at 600-800°C in a fluidized bed, leading to the production of 1,1,1-trichloroethane. Photochemical chlorination of 1,1-dichloroethane at 125°C also produces a high yield of 1,1,1-trichloroethane.

An excellent solvent for oils and grease, which does not attack insulating varnish, 1,1,1-trichloroethane is preferred for cleaning electrical machines, electronic devices and precision instruments. It is also a good dry cleaning agent and is further suitable as an aerosol propellant additive (to reduce costs) and as a constituent in rubber-containing adhesives (Lit.14).

1,1,1-Trichloroethane may be regenerated or recovered by distillation. This can be done on the premises by the user of the solvent or by contract distillation

(Lit.15). Therefore, 1,1,1-trichloroethane is normally not found in concentrated amounts in flows of waste. During production or regeneration a distillation residue sludge is produced, which contains 1,1,1-trichloroethane in various amounts.

Waste Treatment

Mixtures of solvents and highly impure solvents which cannot be regenerated should be turned over to special waste incinerators. Because of the possible emission of harmful vapours during destruction of large amounts, burning at sea is an alternative. Bottom sludge from distillation and other solvent-containing sludge should also be turned over to special waste incinerators. Small quantities of compact distillation sludge may be deposited in sanitary land fills (Lit.16).

Literature

1) Adams, E.M., Spencer, H.C., Rowe, V.K. und Irish, D.D. Arch. Industr. Hyg. I, 225 (1950)

2) Dornette, W.H.L. und Jones, J.P. Anesth. Analg. 39, 249 (1960)

3) Torkelson, T.R., Oyen, F. McCollister, D.D. und Rowe, V.K. Amer. industr. Hyg. Ass. J. 19 353 (1958)

4) Rowe, V.K. Wajkowski, T., Wolf, M.A. Sadek, S.E. und Stewart, R.W. Amer. industr. Hyg. Ass. J. 24, 541 (1963)

5) Steward, R.D., Gay, H.H., Schaffer, A.W., Erley, D.S. und Rowe, V.K. Arch. environm. Hlth. 19, 467 (1969)

1,2-Dichloroethane

DICHLOROETHANE

Formula $C_2H_4Cl_2$ $ClCH_2CH_2Cl$ **CAS no.** 107062

Synonyms ethylene dichloride, ethylene chloride

Appearance	colourless, oily liquid with chloroformlike odour
Melting point	-36°C
Boiling point	83.7°C
Vapour pressure	65 torr at 20°C
Density	1.25 g/cm^3
Vapour density ratio (air = 1)	3.42
Solubility in water	slightly soluble (8.6 g/l)
Flash point	13°C
Ignition temperature	440°C
Inflammable mixture	6.2 - 16 vol.°/o

Toxicity range for short-term exposure:

Man	0.5 - 5 g/kg
Warm-blooded animals	0.7 - 5.8 g/kg
Fish	150 - 175 mg/l
Lower water organisms	1 - 10 mg/l bact.

Occupational safety - Danger symbols F + Xn

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	80	200	25	8				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
		10				

Remarks

1 mg/m^3 ≙ 0.243 ppm
1 ppm ≙ 4.11 mg/m^3

DICHLOROETHANE

Description of Material

1,2-Dichloroethane is a colourless, oily liquid with a chloroformlike odour and a sweetish, burning taste. Its solubility in water is very low, but it dissolves well in alcohol and ether.

In daily applications dichloroethane plays a role as a solvent (stain remover, face lotion and pesticide).

In addition, it is a highly reactive chlorohydrocarbon which is used in many different ways in the chemical industry (see vinyl chloride).

Hazards to Man

The action of 1,2-dichloroethane is similar to that of chloroform and carbon tetrachloride. Poisonings have occurred primarily by accidental swallowing of stain removers and face lotions containing dichloroethane, but also by inhalation of concentrated vapours in industrial plants.

A two-phase manifestation of poisoning is characteristic. Narcotic-type states appear first, accompanied by headaches, nausea as well as distinct excitation and irritation states, which may at high concentrations proceed fast to a deep and sometimes lethal unconsciousness (death through respiratory paralysis) (Lit.1).

Prevalent in the second phase is a gastrointestinal disorder combined with frequent vomiting, bloody diarrhea and abdominal colics. In addition, serious liver and kidney damage develops. In this state death may occur through collapse of the circulatory system, liver coma or anuria with uraemia (Lit. 2).

If the poisoning effects are overcome, persistent damage such as irreversible damage of the brain and nervous system frequently remains(Lit.3).

Chronic poisonings through inhalation of small concentrations over a period of months cause disturbances such as central-nervous depressions, gastrointestinal troubles and neurovegetative disturbances (Lit.4,5).

It is assumed that man can tolerate without ill effects 200 ppm for 7 hours, 1000 ppm for 1 hour and 3000 ppm for 6 min. (Lit.6).

The olfactory threshold is 3-6 ppm (Lit.7).

Hazards to the Environment

Inhalation experiments with mammals (mice, rats, guinea pigs, rabbits, dogs, cats, monkeys) showed that although 1,2-dichloroethane is a strong narcotic compared to carbon tetrachloride and chloroform, it is less toxic than these two chlorohydrocarbons.

Nevertheless, the pathological-histological findings after acute as well as chronic poisoning show the typical effects of chlorohydrocarbon poisoning: characteristic liver and kidney damage, fattening and necrosis of the heart muscle, pulmonary edema, pathological changes of stomach and intestine mucous membranes (Lit.8).

Test doses were in the range of 12 000 and 100 ppm, 7 hours per day and 5 days per week up to the death of the animal.

With doses of 400 ppm most animals died within a short time; only dogs survived 8 months. 200 ppm were tolerated without detectable damage only by rabbits and monkeys, 100 ppm by all animals studied (Lit.9).

For fish (sea perch) an LC_{50} of 150-175 mg/l was determined (Lit.10).

Production and Use / Waste Formation

1,2-Dichloroethane is produced from ethylene and gaseous chlorine or from acetylene and hydrogen chloride. Also, ethylene-containing cracking gases can be used as raw material for this process. More recently, oxychlorination of ethylene ($HCl + O_2$) with copper chloride and ferric chloride catalysts has been used frequently.

Dichloroethane is used as an extracting agent for fats and oils, as a solvent for resins, asphalts, bitumen, and rubber, as a cauterizing agent etc. The bulk of the dichloroethane produced is further processed to vinyl chloride.

Wastes containing 1,2-dichloroethane are produced mainly from its use as a solvent and extracting agent. In most cases they can be regenerated by fractional distillation methods, so that only bottom sludge remains as waste from these operations. Other sources are the spent catalysts from production and processing. During vinyl production, sludge residues are produced which cannot be regenerated (Lit.11).

Waste Treatment

Concentrated wastes, such as distillation residues, spent catalysts and complex sludges, are disposed of in special waste incinerators, since phosgene is liberated during burning of 1,2-dichloroethane. Solvent wastes from small-scale users are collected and regenerated by commercial reprocessing businesses.

DICHLOROETHANE

Aqueous wastes which contain dichloroethane (process effluents) are aerated until the volatile chlorohydrocarbon is evaporated (Lit.11). Special attention has to be given to the emission limits.

Literature

1) W. Hueper, C. Smith, Amer J. med Sci 189, 778 (1935).

2) K. Brass: Dtsch. med. Wschr. 553 (1949).

3) H. Stuhlert: Dtsch. med. Wschr. 1542 (1949).

4) McNedly, W.D., G. Fostnedt: J. industry. Hyg. 24, 13 (1942)

5) C. Guerdjikoff, L'intoxication prof. par le dichlorathane, Reggiane Geneve 1955.

6) D. McCollister et al., Arch. industr. Hlth. 13,1 (1956).

7) V. Ryazanov, Arch. environm. Hlth. 5, 480 (1962).

8) H.Th. Hofmann, et al., Naunyn-Schmiedeberg's Arch. exp. Path. Pharmak. 266, 360 (1970).

9) L.A. Heppel: J. industr. Hyg. 28, 133 (1946).

10) McKee, J.E. und Wolf, H.E. eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

11) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 Vols., issued for the EPA, TRW Systems Group, PB 224579, Set/AS, 1 February 1973.

1,2-Dibromoethane

DIBROMOETHANE

Formula $C_2H_4Br_2$ $BrCH_2CH_2Br$ **CAS no.** 106934

Synonyms ethylene dibromide, ethylene bromide

Appearance colourless liquid with chloroformlike odour

Melting point	10°C
Boiling point	131.4°C
Vapour pressure	8.5 torr at 20°C
Density	2.2 g/cm³
Vapour density ratio (air = 1)	6.48
Solubility in water	slightly soluble (4.3 g/l)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	55 - 420 mg/kg
Fish	
Lower water organisms	

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	190	190						II

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	

Remarks Not flammable
Danger of resorption through the skin

1 mg/m³ ≙ 0.13 ppm
1 ppm ≙ 7.6 mg/m³

DIBROMOETHANE

Description of Material

1,2-Dibromoethane is a colourless, highly refractive liquid of chloroformlike odour. It is only slightly soluble in water, but very highly soluble in alcohol and ether. Upon irradiation with light it decomposes slowly, whereby elemental bromine is liberated, which gives the solution a brownish colour.

Hazards to Man

1,2-Dibromoethane is a weaker narcotic, but stronger toxic substance than 1,2-dichloroethane. In contrast to the chlorine compound, the bromine compound is resorbed through the skin. It causes irritation of skin and mucous membranes. At places where skin resorption has occurred, local edemas and necroses may develop. Inhaled vapours lead to irritation, such as headaches, vomiting, general weakness, gastrointestinal troubles and circulatory collapse, typical of chlorohydrocarbons. Also, damage to organs as described for 1,2-dichloroethane is normal.

Poisonings by 1,2-dibromoethane have occurred mainly through inappropriate application of the material as a pesticide (disinfectant for seed).

Hazards to the Environment

Through its use as a pesticide 1,2-dibromoethane represents a hazard to surface waters. Particularly endangered are cattle grazing near treated agricultural areas.

The LD_{50} value for fresh-water fish is in the range of 15-18 mg/l (Lit.1).

1,2-Dibromoethane injected into the scrotum of bulls shows mutagenic effects (Lit.2,3).

For the same reason disinfected seed should not be fed to laying hens (Lit.4).

Production and Use / Waste Formation

1,2-Dibromoethane is produced from ethylene and bromine or acetylene and hydrogen bromide.

It is used technically as an antiknock agent in fuels in addition to tetraethyllead, as a solvent for synthetic resins and as an intermediate in chemical synthesis.

1,2-Dibromoethane wastes originate at the producer as well as in businesses where the substance occurs as an intermediate during synthesis. Further sources of waste are motor fuel producers, manufacturers of pesticides as well as agricultural users, who employ it as a disinfectant for seed and for soil disinfection (Lit.5).

Waste Treatment

1,2-Dibromoethane has a very low solubility in water and can be removed from effluents by gravity separators settling ponds (Lit.6).

Small remainders may be removed by aerating the water, whereby the harmful material evaporates. The gases which form during this process have to be burnt in special waste incinerators, because during decomposition of 1,2-dibromoethane hydrogen bromide is liberated. However, this action will only be necessary if the emission of hydrogen bromide rises above the permitted level (Lit.7).

DIBROMOETHANE

Literature

1) "Water Quality Criteria Data Book", Vol. 1, Organic Chemical Pollution of Freshwater, EPA Report No. 18010 DPV 12/70, A.D. Little, Inc. December 1973.

2) "Alternatives to the Management of Hazardous Wastes at National Disposal Sites", Report No. C-74861 to EPA, A.D. Little, Inc. May 1973.

3) Malling, Genetics Vol. 61, 39 (1961).

4) Alumot, Residue Rev. 41 (1971).

5) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 Vols., issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973.

Ethylene Chlorohydrin

ETHYLENE CHLOROHYDRIN

Formula C_2H_5ClO $ClCH_2CH_2OH$ **CAS no.** 107073

Synonyms 2-chloroethanol, 2-chloroethyl alcohol, glycol chlorohydrin

Appearance colourless, viscous substance with etherlike odour

Melting point	-67.5°C
Boiling point	128°C
Vapour pressure	4.9 torr at 20°C
Density	1.2 g/cm
Vapour density ratio (air = 1)	2.78
Solubility in water	very soluble
Flash point	55°C
Ignition temperature	425°C
Inflammable mixture	5 - 16 °/o

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	72 - 110 mg/kg
Fish	5 mg/l no effect
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	16	16						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	

Remarks Danger of resorption through the skin

1 mg/m³ ≙ 0.31 ppm
1 ppm ≙ 3.2 mg/m³

ETHYLENE CHLOROHYDRIN

Description of Material

Ethylene chlorohydrin is a colourless liquid with an etherlike odour and a glycerollike consistency. Chemically the compound belongs to the glycol derivatives. The terminal chlorine atom can be readily substituted and hydrolyzed.

Hazards to Man

Ethylene chlorohydrin is a strong poison, because upon contact with the skin and mucuos membranes it hydrolizes immediately and liberates hydrochloric acid. According to the lethal cases that so far have been described in the literature, it appears to attack mainly the lungs and the central nervous system, whereby the effect caused by repeated exposure is cumulative (Lit.1). Inhalation of vapours results first in severe irritation of mucous membranes, especially of the eyes, combined with complaints such as dizziness, headache and vomiting. Even if the first symptoms had been weak, after a latency period of hours there may develop difficulty in breathing, restlessness, gastrointestinal troubles, delirium and cramps and finally pulmonary or cerebral edemas. Also, liver and kidney damage has been observed.

Lethal doses of the compound may be resorbed through the intact skin. Upon oral intake the central nervous system is quickly paralyzed.

For these reasons, industry is attempting to replace this dangerous material by less toxic substances.

Hazards to the Environment

No details are known about injurious effects on plants and animals.

Production and Use / Waste Formation

On a technical scale ethylene chlorohydrin is produced from ethylene and hypochloric acid (HOCl), which in turn is prepared from calcium hypochlorite and gaseous chlorine in an aqueous phase or directly by reacting chlorine with water under pressure. Production from ethylene glycol by heating in the presence of hydrogen chloride is of less importance.

Ethylene chlorohydrin is used as a solvent for cellulose acetate, ethyl cellulose as well as acidic and basic dyes.

It is further an important intermediate product in the synthesis of ethylene oxide, ethylene glycol, insecticides, anaesthetics and plasticizers.

After 1945 the substance was applied in California on a large scale to freshly harvested potatoes to interrupt the germination pause, which normally lasts 90 days, so that the potatoes could be used as seed immediately after harvesting (Lit.2).

Ethylene chlorohydrin wastes are obtained primarily from its use as a solvent and during the production of ethylene oxide and ethylene glycol.

Waste Treatment

Diluted effluents containing ethylene glycol, ethylene oxide and ethylene chlorohydrin may be piped into a sewage treatment plant and biodegraded. Concentrated wastes have to be turned over to special waste incinerators with flue gas scrubbing (Lit.3). Larger quantities may be burnt at sea.

Literature

1) Goldblatt, M.W. und Chiesman, W.E.: Brit. J. industr. Med. 1,207, 1944.

2) Bush, A.F. et al.: J. industr. Hyg. 31, 352 (1949).

3) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutrilization, Recovery or Disposal of Hazardous Waste", 16 Vols., issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973.

Allyl Chloride

ALLYL CHLORIDE

Formula C_3H_5Cl CH_2CHCH_2Cl **CAS no.** 107051

Synonyms 3-chloroprene, 3-chloropropylene

Appearance colourless liquid of pungent odour

Melting point	-136°C
Boiling point	45°C
Vapour pressure	295 torr at 20°C
Density	0.94 g/cm^3
Vapour density ratio (air = 1)	2.64
Solubility in water	slightly soluble (3 g/l at 20°C)
Flash point	$<$-30°C
Ignition temperature	390°C
Inflammable mixture	3.2 - 11.2 °/o

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	24 - 48 mg/l
Lower water organisms	180 mg/l

Occupational safety - Danger symbols F + T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
	3	3						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group
		0.15				

Remarks Danger of resorption through the skin

1 mg/m^3 ≙ 0.33 ppm
1 ppm ≙ 3 mg/m^3

ALLYL CHLORIDE

Description of Material

Allyl chloride is a colourless to strawberry-coloured liquid with a pungent odour. It is only slightly soluble in water, but freely soluble in alcohol. Due to its structural properties (vinyl group and terminal chlorine atom) the compound is very reactive and is widely usable as a starting material and intermediate in organic synthesis.

Hazards to Man

Allyl chloride is a lipoid-soluble substance. It can be resorbed by the intact skin; extended contact with skin leads to inflammation and burns. Inhalation of vapours results primarily in strong irritation of mucous membranes. Accumulation of the compound in nerve tissue quickly leads to headaches, dizziness and at higher concentrations (300 ppm) to unconsciousness. In addition, a highly dangerous pulmonary edema develops.

Chronic disorders include pathological changes of the liver and kidney (Lit.1).

Hazards to the Environment

In water, allyl chloride is slowly hydrolized to allyl alcohol. The LD_{50} for fish is between 24 and 48 mg/l (Lit.2).

For lower organisms (bacteria) the danger threshold is near 180 mg/l (Lit.2).

Production and Use / Waste Formation

Industrially, allyl chloride is produced by direct high-temperature chlorination of propylene or by reaction of allyl alcohol with hydrogen chloride under pressure.

It is used for the production of glycerol, of allyl substituted dyes, pharmaceuticals (mustard oil, sedatives, anaesthetics), and insecticides.

Increasing importance is attached to the synthesis of allyl esters, which are further processed in the plastics industry.

During the synthesis of allyl chloride only effluents generally carry this substance. With the exception of defective batches, practically no concentrated wastes occur. These would definitely have to be turned over to special waste treatment plants in case they are not reprocessed internally. This also holds for smaller quantities from the production of glycerol and allyl esters.

Waste Treatment

In aqueous wastes allyl chloride is converted after a while to allyl alcohol, which is biodegraded in sewage treatment plants. The concentration of the solution, however, may not exceed 100 ppm, otherwise the micro-organisms will be damaged.

Concentrated wastes are destroyed in special waste disposal facilities (Lit.3).

Literature

1) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 vols., issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973.

2) Al Downing et al., J. Proc. Inst. Sewage Purification, Part 6, 537-554 (1964).

3) Patterson, J.W. und Minea, R.A., "Wastewater Treatment Technology", 2nd ed., issued by the Illinois Institute of Technology for Illinois Institute for Environmental Quality, February 1973.

Methyl Chloride

METHYL CHLORIDE

Formula CH_3Cl **CAS no.**

Synonyms Chloromethane

Appearance colourless gas, slightly sweetish odour

Melting point	-97.7°C
Boiling point	-23.7°C
Vapour pressure	3800 torr at 20°C
Density	0.92 g/m^3
Vapour density ratio (air = 1)	1.78
Solubility in water	slightly soluble (4 g/1/20°C)
Flash point	-24°C
Ignition temperature	625°C
Inflammable mixture	7.8 - 18.5 vol.°/o

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	1 - 10 g/l
Fish	
Lower water organisms	

Occupational safety - Danger symbols F + Xn

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	105	209						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	

Remarks Flammable gas

1 mg/m^3 $\hat{=}$ 0.475 ppm
1 ppm $\hat{=}$ 2.1 mg/m3

METHYL CHLORIDE

Description of Material

At room temperature methyl chloride is a gas with a slightly sweetish odour. The gas burns with a green-rimmed flame. Mixed with air it forms explosive mixtures. With water (moisture of the air) it forms at lower temperatures a snowlike gas hydrate ($CH_3Cl \cdot 6 H_2O$), which decomposes again at +7.5°C.

Methyl chloride is only slightly soluble in water; at higher temperatures, however, it is hydrolized by water. It reacts strongly with magnesium and aluminium to form organometallic compounds, which can be used in chemical synthesis for methylation, also of aromatic compounds.

Hazards to Man

The main hazard in working with methyl chloride lies in the fact that the odour of the gas and its primary irritation effect are quite weak, and therefore dangerous concentrations can be inhaled unnoticed. The intake of the compound takes place almost exclusively through respiratory organs. It is freely soluble in lipoids and reaches the nerve tissue relatively fast from the resorbing mucuos membranes.

Its poisonous effect is based on the fact that hydrochloric acid and methanol are formed during intracellular degradation. Acute poisoning manifests itself in headache, nausea, vomiting, lacrimation, cough etc., which frequently occur after a latency period of 15-24 hours or more.

Subsequent to this, more serious nervous disorders of various kinds occur, e.g. paralysis as well as liver and kidney damage, which may persist over weeks and whose improvement is often interrupted by set-backs. Frequently persistent nervous disorders (trembling) occur, which often prevent any occupational activity (Lit.1).

If the gas in its liquefied form (as a refrigerant) comes in contact with the skin, local freezing and blistering result.

Since methyl chloride belongs to the highly dangerous chlorohydrocarbons, the pungent smelling acrolein is added as a warning substance, if used as a refrigerant. Methyl chloride is stored in steel cylinders under pressure. Upon contact with aluminium the compound ignites immediately in air (Lit.2).

Hazards to the Environment

Methyl chloride appears to be relatively nonpoisonous to animals. Experiments with dogs, which were given aqueous solutions of 5.95 g/l, showed no poisoning symptoms nor a change in the haemoglobin or blood count (Lit.3).

The poisonous concentration for fish is in the range of 1 to 10 g/l (Lit.4).

Production and Use / Waste Formation

Industrially, methyl chloride is produced by

- chlorination of methane
- esterification of methanol with hydrogen chloride.

Methyl chloride is primarily used as a refrigerant in household and small-business refrigeration units.

It is further applied in the gentle extraction of flavouring substances from foodstuffs, as a solvent in low-temperature polymerization, as a solvent and propellant, when pesticides and plant hormones are applied as aerosols. In the chemical industry it is used as a catalyst for the polymerization of butyl rubber, and it is a starting material for the production of silicones, of methylcellulose (cellulose ether, phenol methyl ethers, tetramethyllead and N-methylamine). Other chloromethanes are produced by further chlorination of methyl chloride.

METHYL CHLORIDE

Producers as well as users produce methyl chloride wastes. Larger quantities originate during production of silicones, butyl rubber, tetramethyllead and methylcellulose. Other industrial branches have insignificant amounts of methyl chloride wastes.

Waste Treatment

Larger quantities of methyl chloride are recovered out of economic considerations by low-temperature condensation. Aqueous or other wastes of low concentration are destroyed in special waste incinerators (Lit.5).

Literature

1) Valentin, Klosterkötter, Lehnert, Petry, Rutenfranz, Wittgens, Arbeitsmedizin Thieme Verlag Stuttgart 1971.
2) Hommel, Handbuch der gefährlichen Güter, Springer-Verlag 1973/74.
3) McKee, J.E. und Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.
4) Evaluation of the Hazard of Bulk Water Transportation of Industrial Chemicals, A tentative Guide, National Academy of Sciences 1970.
5) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 vols., issued for the EPA, TRW Systems Group, PB 224579, Set/AS, 1 February 1973.

Carbon Tetrachloride

CARBON TETRACHLORIDE

Formula CCl_4

CAS no. 56235

Synonyms

Appearance colourless liquid of sweetish odour

Melting point	-23°C
Boiling point	76.7°C
Vapour pressure	90 torr at 20°C
Density	1.59 g/cm³
Vapour density ratio (air = 1)	5.5
Solubility in water	very slightly soluble(0.8g/1/20°)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	3 - 12.8 g/kg
Fish	100 - 1000 mg/l
Lower water organisms	(0.8 - 1.6 g/l) Bact.

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	65	65	10	3				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		1.95				M

Remarks Danger of resorption through the skin, 1 mg/m³ = 0.154 ppm
nonflammable gas **61<** 1 ppm = 6.5 mg/m³

Description of Material

Carbon tetrachloride is a waterclear, neutral liquid of sweetish, etherlike odour, which may be differentiated distinctly from that of chloroform. It is nonflammable and at room temperature absolutely stable even in the presence of light and air. Carbon tetrachloride decomposes in flames to hydrogen chloride, carbon and phosgene. At higher temperatures and in the presence of chlorine acceptors it decomposes to chlorine and carbon tetrachloride.

Mixtures of zinc dust and carbon tetrachloride burn after ignition, giving off smoke and fog. With aluminium powder it may explode spontaneously. With alkali, alkaline earth and some light metals carbon tetrachloride forms explosive mixtures sensitive to percussion.

Hazards to Man

Carbon tetrachloride is one of the most dangerous solvents used in industry. Similar to chloroform, carbon tetrachloride acts as a narcotic. Inhalation of high concentrations may lead relatively fast to unconsciousness and death through suspension of breathing.

Lower concentrations (1000-1500 ppm) lead initially to nervous stomach and intestinal disorders with vomiting, diarrhea, colics and fever. In addition, severe liver and kidney damage develops, which is completely restored only after weeks.

In severe cases poisoning leads to death within 1-2 days with all symptoms of a liver coma and uraemia.

Chronic poisonings manifest themselves in less severe troubles, such as headaches, dizziness, noticeable tiredness, loss of appetite and loss of weight. Even in these cases liver and kidney damage may occur, which, however, is not as severe.

Upon continued skin contact, severe dermatoses and in some cases eczematous changes of an allergic nature may occur due to severe defatting of the skin. Long-term exposure to (liquid) carbon tetrachloride leads to burns with blisters and abscesses.

The danger of phosgene formation during burning of carbon tetrachloride has been mentioned before.

Hazards to the Environment

Serial examinations were carried out with mammals, fish and lower organisms.

A daily eight-hour inhalation of 10 cm^3/m^3 causes biochemically detectable liver disorders in small mammals. Liver damage was also detected after improper application of carbon tetrachloride as a vermicide (Seretin) against hookworms and liver flukes in veterinary medicine. The poisonous dose is 1.0 ml for sheep and 0.5 ml for cows (Lit.1).

Carbon tetrachloride caused cancerous growths in mice (Lit.2).

Harmful concentrations to fish lie between 100 and 1000 mg/l (Lit.1).

180 mg/l are harmful to lower water organisms (Lit.3).

Production and Use / Waste Formation

There are a number of methods for the production of carbon tetrachloride, all of which are utilized:

- continued chlorination of low methane chlorination products,
- high-temperature chlorination of methane,
- chlorinating cleavage of ethane, propane, butane etc.,
- chlorination of carbon disulphide and methane.

The latter two are the most effective methods.

Carbon tetrachloride is used as a dry cleaning agent due to its nonflammability and its good solvent properties for oils, fats, resins, pitch, bitumen, tar, asphalt and varnish. In the textile industry it is used instead of benzine as a spot-removing agent for cleaning fabrics, leather and furs. In addition to other chlorinated hydrocarbons it is used for degreasing metals, in particular for degreasing and deoiling delicate small parts (e.g. parts of watches, incandescent filament and circuit parts of telecommunication equipment). In the rubber industry it is used as a swelling agent and solvent for unvulcanized rubber, during cold vulcanization as a diluent for sulphur dichloride. In the chemical manufacturing industry carbon tetrachloride serves as a base for spot removers, floor cleaners and as a solvent for furniture polish and bituminous coating material. Polycompounds such as ethylcellulose, polyacrylic acid, polystyrene paints and chlorinated rubber are dissolved in carbon tetrachloride. Mixed with 20% alcohol it also dissolves acetylcellulose, benzylcellulose and polyvinyl acetate.

In agriculture carbon tetrachloride is applied as a gassing compound for grain storage parasites, for disinfecting agricultural soil and as a solvent for natural (pyrethrum) and synthetic pesticides. Carbon tetrachloride is further processed chemically on a large scale to fluorochloromethanes, which are commercially traded as Freons or Frigens. Carbon tetrachloride gives satisfactory results as a solvent in Friedel-Crafts reactions and is useful for solvent extraction.

In all the above-mentioned production and processing methods various amounts of wastes containing carbon tetrachloride are produced. Large amounts are obtained particularly from dry cleaning operations, during degreasing and from synthetic processes.

Waste Treatment

Most of the large-scale consumers recover impure solvents by distillation. Small-scale consumers take their spent material to commercial solvent recovery businesses. Residues from recovery operations are turned over to special waste dumps or are burnt in special waste incinerators.

Literature

1) McKee, J.E. und Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

2) "Water Quality Criteria Data Book", Vol. 1, *Organic Chemical Pollution of Freshwater*, EPA Report No. 18010 DPV 12/70, A.D. Little, Inc. December 1973.

3) Liebmann, H., Handbuch der Frischwasser- und Abwasserbiologie vol. 2, Munich, R. Oldenbourg 1960.

Chloroprene

CHLOROPRENE

Formula C_4H_5Cl $CH_2=CCl-CH=CH_2$ **CAS no. 126 998**

Synonyms 2-chlorobutadiene-(1,3), chlorobutadiene

Appearance

Melting point	-130°C
Boiling point	59.4°C
Vapour pressure	200 torr
Density	0.958 g/cm³
Vapour density ratio (air = 1)	3
Solubility in water	very slightly soluble
Flash point	-20°C
Ignition temperature	
Inflammable mixture	2.5 - 20 vol. °/o

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	36	92						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	

Remarks

1mg/m³ ≙ 0.272 ppm
1 ppm ≙ 3.680 mg/cm³

CHLOROPRENE

Description of Material

Chloroprene is a colourless, volatile liquid of ether-like odour, similar to ethylbromide. The solubility in water is low; it is, however, miscible with most organic solvents. Due to its two double bonds, it is very reactive. Even in the absence of light it polymerizes spontaneously at room temperature. Several inorganic and organic compounds undergo addition upon irradiation with light, partly with an explosionlike reaction. For this reason stabilizers (e.g. p-tert-butyl-catechol, phenothiazine) have to be added to monomeric chloroprene. It has to be stored and transported cooled to -10°C under an inert gas atmosphere with less than 10 ppm oxygen. During storage of chloroprene in the presence of stabilizers, dimers are formed as a function of time. Under certain conditions highly undesirable, so-called popcorn polymers are formed, which are insoluble in the monomer. The rate of growth of these popcorn polymers is proportional to the existing amount. A popcorn polymer contains, due to its spongelike nature, many monomers and may ignite spontaneously during storage in air.

Hazards to Man

Inhalation of chloroprene vapours as well as direct skin contact cause harmful reactions in man.

Low concentrations of chloroprene (about 80 ppm) affect the central nervous system and cause depressive moods accompanied by headaches, tiredness, nervousness, drop of blood pressure, loss of appetite, chest pains and disturbances of the heart rhythm. It was detected that chloroprene acts on enyzmes with mercapto terminal groups, e.g. adenosine-triphosphatase, xanthine-oxidase, succinic dehydrogenase, hexokinase and choline esterase. Upon long-term exposure loss of hair on the head and eyebrows as well as slower growth of the beard occur.

The symptoms regress some time after termination of the exposure.

Repeated inhalations result in damage to the liver, kidney and, especially, lungs.

Higher concentrations (no exact data) lead within a few seconds to a collapse and after 3-4 minutes to death with acute pulmonary edema.

Liquid chloroprene is resorbed through the outer skin and leads to local skin and mucous membrane irritations. Concentrated vapours cause conjunctivitis and changes in the cornea (Lit.1).

Hazards to the Environment

Serial examinations of acute effects were carried out with mammals. Corresponding experiments to clarify the chronic effect of chloroprene on mammals are still continuing.

An eight-hour inhalation of 165 ppm for rats, 355 ppm for cats and 1064 ppm for rabbits resulted in death of all animals. With mice a one-hour inhalation of 825 ppm led to the same result.

Skin contact with chloroprene at a dose of 435 mg/kg was lethal for 85% of the tested animals (cats) (Lit.2).

Production and Use / Waste Formation

Chloroprene is produced technically by two processes:

1. From acetylene and hydrogen chloride.

This method converts acetylene catalytically in an intermediate step to monovinylacetylene, to which hydrogen chloride is added to form chloroprene. Due to the high energy consumption this method has become uneconomical.

2. From butadiene and chlorine.

The addition of chlorine to butadiene produces as intermediate products dichlorobutenes, which after isomerization via catalytic dehydrohalogenation are converted to chloroprene. This process is favoured by the unavoidable production of butadiene in ethylene plants and is almost exclusively used today because of its economic advantages.

Because it polymerizes easily, chloroprene is polymerized in emulsion to products with valuable technical properties. Due to its resistance to sunlight, oxygen and mineral oils and its flame resistance, chloroprene rubber has many and varied applications as a special material with the good properties of natural rubber. Due to the above-mentioned resistance properties, chloroprene has various applications in the rubber and adhesive industries (products made of polychloroprene, e.g. conveyor belts in underground mines, window profiles, bridge supports, V-belts, gaskets, mining and deep-sea cables, further as an adhesive).

Chloroprene-containing wastes are produced during production and distillation of chloroprene and during emulsion polymerization through product separation and popcorn formation in reactors or bottoms of distillation towers.

Waste Treatment

Due to their high reactivity and volatility chloroprene and chloroprene-containing wastes cannot be dumped. Therefore, if the chloroprene cannot be distilled, the wastes have to be destroyed in special waste incinerators. Because of the large quantities of chlorine present in exhaust gases during incineration, the flue gases have to be scrubbed.

Literature:

1) Henschler "Gesundheitsschädliche Arbeitsstoffe" 4th edition (1975), Verlag Chemie Weinheim

2) Journal of Industrial Hygiene and Toxicology (Baltimore / New York)

quoted in: Christensen et al.: "The toxic Substances list; 1974, US Department of Health, Education and Welfare, Rockville, Maryland 20252, June 1974

3) Ullmanns Encyklopädie der Technischen Chemie, 4th edition, Vol. 9, Verlag Chemie, Weinheim 1975

4) Winnacker/Küchler "Chemische Technologie", 3rd edition, Vol. 4, Carl Hauser Verlag, München 1972

5) Kirk-Othmer "Encyclopedia of Chemical Technology" 2. Ed., Vol 5, John Wiley & Sons, Inc. New York, London, Sydney, 1964

6) Beilstein "Handbuch der Organischen Chemie" 4th edition, 3rd supplement, Vol. I, Part 1 Springer Verlag Berlin, Göttingen, Heidelberg 1958

7) Houben-Weyl, "Methoden der organischen Chemie", Band XIV/1, Makromolekulare Stoffe, Teil 1, Georg Thieme Verlag, Stuttgart 1961 - p. 733 ff.

8) Bayer, "Handbuch für die Gummiindustrie", edited by: Bayer AG - Kautschukanwendungstechnik, 1971

Dichlorodiisopropyl ether

DICHLORODIISOPROPYL ETHER

Formula $C_6H_{12}Cl_2O$ $CH_2Cl\text{-}CH(CH_3)_2O$ **CAS no.** 108 601

Synonyms 2,2-dichloroisopropyl ether,
di-(2-chloro-1methyl-ethyl) ether

Appearance clear liquid of pleasant odour

Melting point	
Boiling point	187 °C
Vapour pressure	0.1 torr
Density	1.103 g/cm^3
Vapour density ratio (air = 1)	3.8
Solubility in water	slightly soluble (1.4 g/l)
Flash point	85 °C
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	240 - 3000 mg/kg
Fish	
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	

Remarks

DICHLORODIISOPROPYL ETHER

Description of Material

Dichlorodiisopropyl ether is a colourless liquid of pleasant odour. In water it is slightly soluble. The solubility in most organic solvents is practically unlimited (Lit.3).

Hazards to the Environment

Serial examinations have been carried out with mammals.

Oral intake of a dose of 240 mg/kg by rats and 3000 mg/kg by rabbits caused death to 50% of the tested animals. A five-hour inhalation of a concentration of 700 ppm caused death within 24 hours to rats (Lit.1).

Production

Dichlorodiisopropyl ether is a byproduct (1.5-2%) in propylene oxide production by the chlorohydrin process. Presumably it is also a byproduct in other, more recent methods in the synthetic resin or similar industries (Lit.2).

Waste Treatment

Like almost all halogen hydrocarbon wastes dichlorodiisopropyl ether wastes are destroyed in special waste incinerators. Due to the high hydrogen chloride content of the flue gases incineration takes place predominantly at sea.

Literature

1) American Medical Association Archives of Industrial Hygiene and Occupational Medicine (Chicago)
British Journal of Industrial Medicine (London)
quoted in: Christensen et. al "The Toxis Substances List" 1974 US Department of Health, Education and Welfare Rockville, Maryland 20852 June 1962

2) Winnacker/Küchler "Chemische Technologie", 3rd edition, Vol. 4 Carl Hanser Verlag Munich1972

3) Beilstein "Handbuch der Organischen Chemie" 4th edition, 3rd supplement, Vol.1, Part 1 Springer-Verlag Berlin, Göttingen, Heidelberg.

1,2-Dichloropropane

DICHLOROPROPANE

Formula $C_3H_6Cl_2$ $CH_3-CHCl-CH_2Cl$ **CAS no.** 078 875

Synonyms propylene chloride

Appearance	colourless liquid of sweetish, chloroformlike odour
Melting point	-100.4°C
Boiling point	96.5°C
Vapour pressure	42 torr
Density	1.15 g/cm³
Vapour density ratio (air = 1)	3.9
Solubility in water	very slightly soluble
Flash point	15°C
Ignition temperature	600°C
Inflammable mixture	3.4 - 14.5 vol. °/o

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	860 - 5000 mg/kg
Fish	
Lower water organisms	

Occupational safety - Danger symbols F, Xn

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	350	350						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	

Remarks Isomers : 1,1-dichloropropane CAS No 078 999 1,3-dichloropropane

1mg/m³ ≙ 0.214pp
1ppm ≙ 4.67mg/m³

1,2 - DICHLOROPROPANE

Description of Material

1,2 - Dichloropropane is a colourless, highly fluid liquid of sweetish, chloroformlike odour. It is virtually insoluble in water, but soluble in most organic solvents. In the dry state it is stable and can be stored without stabilizers. As a highly volatile and ignitable substance it forms explosive mixtures with air. The vapours are considerably heavier than air (Lit.5).

Hazard to Man

Like almost all halogen hydrocarbons 1,2-dichloropropane is a respiratory and contact poison. Inhalation of vapours leads to irritation of the respiratory tract, headaches, nausea, dizziness and in severe cases loss of consciousness.

Repeated exposures over a longer period cause liver, kidney and heart damage.

Local contact leads to irritations and in severe cases to inflammation of the skin.

In spite of its varied uses in industry, no occupational diseases from 1,2-dichloropropane have become known (Lit.1).

Hazards to the Environment

Serial examinations have been conducted with mammals. A six-hour inhalation of 1000 ppm repeated twenty times did not lead to toxic effects in rats, however, liver damage was detected after dissection. Dogs withstood a seven-hour inhalation of 400-500 ppm over 140 days without damage to organs. Feeding a dose of 1900 mg/kg to rats and 850 mg/kg to mice caused death in 50% of the tested animals (Lit.2,3).

1,2 - DICHLOROPROPANE

Production and Use

1,2-Dichloropropane is formed in large quantities (10-15 %)as a byproduct in the production of propylene oxide by the chlorohydrin process. It may be produced in high yields by the addition of chlorine to propane. 1,2-Dichloropropane is also formed as a byproduct during hot-chlorination of propane.

It is used extensively as a solvent for resins, waxes, fats, oils, gums and rubber in the respective branches of industry. Since it dissolves readily bitumen, asphalt and tar, it is used in the production of protective material for construction and of tarpapers.

In line with its use as a solvent, dichloropropane-containing waste are produced especially during production and processing of synthetic resins and protective material for construction, as well as in the rubber industry (Lit.3,4).

Waste Treatment

Due to their volatility and inflammability, 1,2-dichloropropane and dichloropropane-containing wastes cannot be dumped. They therefore have to be destroyed in special waste incinerators. Because of the high content of hydrogen chloride and possibly phosgene in the flue gases, extensive safety and cleaning precautions have to be taken. Dichloropropane-containing wastes are, therefore, generally burnt at high sea.

Literature

1) Kühn-Biret
"Merkblätter Gefährliche Arbeitsstoffe", Verlag Moderne Industrie Munich 1975

2) Journal of Industrial Hygiene und Toxicology (Baltimore/New York)

American Industrial Hygiene Association (Baltimore)

American Journal of Hygiene (Baltimore)

Encyclopedia of Chemicals and Drugs Merck Co., Incl. Rahwag, New Jersey

Quoted in: Christensen et al.: "The Toxic Substances List" 1974, US Department of Health, Education and Welfare, Rockville, Maryland 20852, June 1974

3) "Ullmanns Encyclopädie der Technischen Chemie" 4th edition, Vol. 9, Verlag Chemie Weinheim

4) Winnacker/Küchler "Chemische Technologie" 3rd edition Vol. 4, Carl Hanser Verlag Munich 1972

5) Beilstein "Handbuch der Organischen Chemie", 4th edition, 3rd supplement, Vol. I, Part 1 Springer Verlag Berlin, Göttingen, Heidelberg 1958

B ORGANIC SULPHUR, NITROGEN, NITRO AND PHOSPHOROUS COMPOUNDS, EXCLUDING BIOCIDES

B 1 Aniline
B 2 Nitrotoluene
B 3 Nitrobenzene
B 4 Chloronitrobenzene
B 5
B 6
B 7
B 8
B 9
B10
B11
B12
B13
B14
B15
B16
B17
B18
B19
B20

Aniline

Formula C_6H_7N $C_6H_5NH_2$ **CAS no.** 62533

Synonyms aminobenzene, phenylamine, aniline oil, aminophen

Appearance oily, colourless to brown liquid with a characteristic odour

Melting point	-6°C
Boiling point	184°C
Vapour pressure	2.4 torr at 20°C
Density	1.02 g/cm^3
Vapour density ratio (air = 1)	3.22
Solubility in water	soluble (30 g/l at 20°C)
Flash point	76°C
Ignition temperature	approx. 530°C
Inflammable mixture	1.3 - 11 vol. %

Toxicity range for short-term exposure:

Man	50-500 mg/kg
Warm-blooded animals	0.5-2.5 g/kg
Fish	3-100 mg/l
Lower water organisms	0.4-280 mg/l

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	19	19	2.4	0.8				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.95				

Remarks Danger of resorption through the skin 1 mg/m^3 = 0.265 ppm
1 ppm = 3.8 mg/m^3

ANILINE

Description of Material

Freshly distilled aniline is a colourless oil of characteristic odour, which due to autooxidation, soon turns brown in air. The commercial substance normally contains impurities such as benzene, nitrobenzene or toluene. Aniline is soluble in water and volatile with steam. It has a weak basic character and forms salts with strong mineral acids.

Hazards to Man

Aniline is a potent blood and nerve poison. It normally gets into the body via resorption through the skin, less frequently through inhalation of vapours or through oral intake. Elevated temperature and moist skin increase the rate of resorption. Acute poisoning manifests itself in a relatively fast grey-blue discoloration of the skin, along with definite euphoric side effects (aniline pip). The symptoms of the advanced state of poisoning are nausea and vomiting, headaches, difficulty in breathing, slackening of heartbeat, bloody urine, in some cases cramps. Chronic poisoning frequently manifests itself merely in tiredness, loss of appetite, and general weakness combined with loss of weight.

When handling aniline, direct contact with the skin has to be definitely avoided (protective clothing, breathing protection). After an accident all affected clothing has to be removed. The skin has to be washed carefully with water or 5% acetic acid (no alcohol, it augments the action of aniline).

Aniline is combustible. Upon heating, poisonous vapours, at higher temperatures explosive mixtures, are formed. Ignition may occur at hot surfaces, by sparks or open flames. Aniline, therefore, should be stored in well-secured containers, cool and with good ventilation.

ANILINE

Hazards to the Environment

The poisonous effect was experimentally verified for plankton, fish and mammals. The danger threshold for algae (Scenedesmus) is 10 mg/1, for small crustaceans (Daphnia) 0.4 mg/1.

Lethal concentrations for fish show wide margins. Values between 100 and 1000 mg/1 have been found (Lit.2). Oral doses of 0.5-2.5 g/kg are toxic to mammals (Lit.3).

Production and Use / Waste Formation

Aniline, the base compound of aromatic amines, is produced on a technical scale by reduction of nitrobenzene with iron and water in the presence of hydrochloric acid. More recently, the pressureless catalytic hydrogenation of nitrobezene in the gas phase on a copper contact has partly replaced the reduction with iron.

Aniline is an important starting material in the synthesis of dyes (aniline dyes), pharmaceuticals (sulphonamides, synthetic sweeteners), isocyanate polymers, rubber chemicals, preservatives, vulcanization accelerators, photochemicals (hydroquinone) and cyclohexylamine, an important intermediate for polyamide production.

In the aniline producing as well as processing industries various amounts of aniline wastes can be expected, especially in waste waters. This holds in particular for dye, varnish and rubber producers, but also for chemical plants and gas producers (Lit.4).

ANILINE

Waste Treatment

Diluted aqueous solutions may be treated in biological sewage treatment plants after prior acclimatization of the activated sludge. Larger amounts of concentrated aniline wastes have to be destroyed in special waste incinerators.

Literature

1) Bringmann, G., Kühn, R.
Vergleichende Wassertoxikologische Untersuchungen an Bakterien, Algen, Kleinkrebsen.
Gesundheitsing. 80 115 - 119 (1959)

2) McKee, J.E. und Wolf, H.E., eds.,
"Water Resources Control Board, Publication 3 - A 1963

3) Gelsenkirchener Dokumentation,
Hygiene-Institut des Ruhrgebietes, Gelsenkirchen, 1973

4) "Water Quality Criteria Data Book, "Vo. 1, Organic Chemical Pollution of Freshwater
EPA Report No. 18010 DPV 07/71,
A.D. Little, Inc. Juli 1971

5) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste" issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973.

Nitrotoluene +)

NITROTOLUENE

Formula $C_7H_7NO_2$ $NO_2C_6H_4CH_3$ **CAS no.** 887220

Synonyms nitromethylbenzene

Appearance pale yellow liquid with a weak odour resembling that of oil of bitter almond

Melting point	-4°C
Boiling point	222°C
Vapour pressure	1 at 50°C
Density	1.16 g/cm^3
Vapour density ratio (air = 1)	4.73
Solubility in water	very slightly soluble
Flash point	106°C
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	18 - 40 mg/l
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	30							II

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group

Remarks +) 3 isomers: 1,2 (o-)-nitrotoluene CAS-No. 887220
1,3 (m-)-nitrotoluene CAS-No. 99081
1,4 (p-)-nitrotoluene CAS-No. 99990

82<

NITROTOLUENE

Description of Material

Nitrotoluene forms 3 isomers:

1,2 - nitrotoluene (ortho-compound)
1,3 - nitrotoluene (meta-compound)
1,4 - nitrotoluene (para-compound)

A characteristic technical product comprises about 63% o-nitrotoluene, 4% m-nitrotoluene and 33% p-nitrotoluene. All three isomers may be isolated, but of technical importance are only the isomer mixture and the o- and p-compounds. o- and m-nitrotoluenes are yellow liquids with a weak odour resembling that of oil of bitter almond. p-Nitrotoluene forms colourless crystals. All three are slightly soluble in water, but readily soluble in benzene, chloroform, acetone, alcohol, ether as well as in most other organic solvents.

Hazardsto Man

Nitrotoluene is readily resorbed through the skin. Contaminated clothing has to be removed immediately. Due to its low solubility in water, the poisoning effect occurs only after 1 - 3 hours. Alcohol aggravates the effect. In addition to strong vomiting there are initially headaches, dizziness and unconsciousness. In severe cases death occurs through respiratory paralysis after a deep coma. Signs of severe poisoning are a blue-grey discoloration of the skin, especially of mucous membranes, and a chocolate brown discoloration of the blood. Upon chronic exposure disturbances in blood formation in addition to liver and kidney damage can be observed.

Upon heating to a high temperature, explosive mixtures are formed, which can be ignited at hot surfaces, by sparks or open flames. Upon heating to decomposition or by burning, highly poisonous nitrous gases are produced.

NITROTOLUENE

Hazards to the Environment

The minimum lethal dose (MLD, LD_{25}) for minnows is in distilled water 18 to 20 mg/l, in hard water 35-40 mg/l (Lit.1). The poisonous effect of the para compound is lower than that of the ortho compound (Lit.2).

Production and Use / Waste Formation

All three isomers are formed simultaneously by nitration of toluene. A mixture of 63% o-, 33% p- and 3-4% m-nitrotoluene is obtained, which may be separated by a combination of distillation, freezing and centrifugation.

Nitrotoluene as such is little used in the chemical industry. It is a typical intermediate for the production of dyes (New Fuchsin, Turkey Blue), polymers, fragrances and explosives.

During the production of nitrotoluence waste waters of low concentration are formed at wash and precipitation steps. Wastes of higher concentration are residues from distillation columns.

Waste Treatment

Aqueous waste waters with low concentrations of nitrotoluene have to be neutralized with lime or undergo a biological pretreatment with activated sludge before being admitted to the drainage ditch.

Wastes with higher concentrations of nitrotoluene are best turned over to an incinerator with nitrogen oxide scrubber.

Literature

1) Gelsenkirchener Dokumentation
Hygiene Instiut des Ruhrgebietes, Gelsenkirchen (1973)

2) Ullmann, Enzyklopädie der Technischen Chemie,
3rd edition, Vol. 12, pp. 768 - 784 (1964)
Verlag Chemie Weinheim

Nitrobenzene

NITROBENZENE

Formula $C_6H_5NO_2$ **CAS no.** 98953

Synonyms nitrobenzol, essence of mirbane,
oil of mirbane

Appearance colourless to pale yellow, oily liquid with odour resembling that of oil of bitter almond

Melting point	6°C
Boiling point	211°C
Vapour pressure	1 mm Hg at 44.4°C
Density	1.20 g/cm^3
Vapour density ratio (air = 1)	4.25
Solubility in water	slightly soluble
Flash point	88°C
Ignition temperature	480°C
Inflammable mixture	1.8-40 vol.% (is not reached under normal conditions)

Toxicity range for short-term exposure:

Man	1-5 g/kg
Warm-blooded animals	0.48-1 g/kg
Fish	20-100 mg/1
Lower water organisms	28 mg/1

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	5		0.85	0.30				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group

Remarks

NITROBENZENE

Description of Material

Nitrobenzene is a colourless to pale yellow, highly refractive liquid with an odour resembling that of oil of bitter almond. It is only slightly soluble in water (2 g/l at 30°C). The aqueous solution tastes extremely sweet. It is highly miscible with alcohols, ethers and benzene.

Nitrobenzene is the most important nitro compound in organic chemistry produced on a large scale for further processing.

Hazards to Man

Nitrobenzene is very easily resorbed through the skin. Nitrobenzene-contaminated clothing can lead to serious and lethal poisonings, if not removed immediately. Upon oral intake a few ml of the liquid may be lethal. Due to the low solubility in water, the poisonous effect appears frequently only after a delay of 1-3 hours. Alcohol aggravates the poisonous effect. In addition to heavy vomiting and severe stomach colics, headaches, dizziness and unconsciousness occur initially. In severe cases death occurs through respiratory paralysis after a deep coma.

Signs of severe poisonings are the intensive bitter almond odour of the breath, a chocolate brown discoloration of the blood and disturbances of the central nervous system. Chronic poisonings are rare. They can lead to liver and metabolic disorders, anaemia and eczematous changes. Upon heating to a high temperature, explosive mixtures are formed, which can be ignited at hot surfaces, by sparks or open flames. Upon heating to decomposition or burning, highly poisonous nitrous gases are produced.

NITROBENZENE

Hazards to the Environment

The minimum lethal dose (MLD,LD_{25}) for minnows is 20 to 24 mg/l in distilled water, 90 to 100 mg/l in hard water (Lit.1).

Production and Use / Waste Formation

Today nitrobenzene is primarily produced by nitrating benzene with nitrating acid (nitric acid/sulphuric acid) at temperatures below 50°C in a continuous operation. As most aromatic nitro-compounds it is primarily used as an intermediate for the production of dyes and explosives. It serves on a large scale as an intermediate for the preparation of aniline, benzidine, quinoline, azobenzene, chloronitrobenzene, nitrobenzenesulphonic acid. Furthermore, it has limited applications as a perfuming agent in the soap industry, as a solvent and oxidizing agent in chemical synthesis.

Nitrobenzene-containing wastes are formed during production after the purification step (water wash, steam distillation) and during processing (mainly to aniline).

Waste Treatment

Aqueous wastes with low concentrations of nitrobenzene have to be neutralized with lime or undergo a biological treatment with activated sludge and subsequent sand filtration before being admitted to the drainage ditch.

Wastes with higher concentrations of nitrobenzene are best turned over to an incinerator with nitrogen oxide scrubber.

Literature

1) Gelsenkirchner Dokumentation
Hygiene-Institut des Ruhrgebiets, Gelsenkirchen (1973)

Chloronitrobenzene | p-CHLORONITROBENZENE

Formula $C_6H_4ClNO_2$ $C_6H_4ClNO_2$ **CAS no.** 000 100 005

Synonyms p-nitrochlorobenzene

Appearance yellow crystals

Melting point	83°C+
Boiling point	242°C+
Vapour pressure	5.44 torr+
Density	1.29 g/cm^3 +
Vapour density ratio (air = 1)	5.43+
Solubility in water	virtually insoluble
Flash point	127°C
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	5 - 50 mg/kg
Warm-blooded animals	400-1400 mg/kg+
Fish	
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	1	1						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	

Remarks Danger of resorption through the skin 1 mg/m^3 = 0.5 ppm
+ data are for p-chloronitrobenzene 1 ppm = 2 mg/m^3

CHLORONITROBENZENE

Description of Material

Chloronitrobenzene exists in three isomeric forms, ortho-, meta- and para-chloronitrobenzene. Of technical importance is mainly p-chloronitrobenzene, to a lesser extent also o-chloronitrobenzene.

p-Chloronitrobenzene crystallizes in yellow monoclinic prisms. The crystals have a characteristic odour, similar to that of nitrobenzene. They are readily soluble in diethyl ether and benzene, soluble in ethanol and insoluble in water. The substance is combustible. Upon heating, poisonous vapours are set free. Chloronitrobenzenes are very reactive compounds. In p- as well as in o-chloronitrobenzene the chlorine atom may easily be replaced by functional groups such as -OH, $-OCH_3$, $-OC_2H_5$, $-OC_6H_5$, $-NHC_6H_5$. For this reason chloronitrobenzenes have a variety of uses in chemical synthesis (Lit. 1.2).

Hazards to Man

Chloronitrobenzene belongs to those aromatic nitro compounds which easily cause sickness upon incorrect handling. This sickness is classified and compensated as an occupational disease according to the 7th occupational disease regulations (Lit.3).

Control of processing companies has to be carried out according to the accident prevention regulations of the professional organization of the chemical industry (regulation for plants in which nitro and amido compounds, dangerous to health, are produced or regularly recovered in larger quantities - VBG 104).

The direct effect upon skin contact is strong irritation of the affected areas with the danger of formation of eczema. The skin has to be cleaned thoroughly as quickly as possible, because the substance is resorbed.

Severe poisoning may result by inhalation of dusts and vapours, less frequently by oral intake. Poisoning symptoms are headaches, nausea, vomiting, colics, excitedness, circulatory trouble, unconsciousness with difficulty in breathing etc. They are frequently accompanied by a typical blue discoloration of the skin (cyanosis) and a change in blood count through development of methaemoglobinaemia. The cause of this disease is the change in the body of chloronitrobenzene to nitrosobenzene, which is known as a methaemoglobin former.

The latency period until the symptoms become apparent may take, depending on the amount absorbed, hours or days. Delayed damage known includes disorders of the kidney function, the central nervous system and longer lasting blood disorders. Also, the repeated intake of small doses leads to damage, since this substance accumulates in the body (Lit.1,4,5,6).

Hazards to the Environment

Hazards presented to the environment by chloronitrobenzene are similar to those of nitrobenzene. Generally, chlorinated nitro compounds are considered highly poisonous (Lit.7). That is particularly true of m-chloronitrobenzene, which is lethal to cats upon repeated inhalations of 8-30 ppm (Lit.1). In small mammals, depending on the species, 400 - 1400 mg/kg are toxic (Lit.8). Upon decomposition by heat and formation of nitrogen oxides and nitric acid, the poisoning of waters may be a possibility during catastrophes. 36 mg $HNO_3/1$ are reported as the toxic threshold for fish (Lit.9).

Production and Use / Waste Formation

The production of chloronitrobenzene on a technical scale takes place by nitration of chlorobenzene with mixed acids (52.5% sulphuric acid, 35% nitric acid and 12% water) at 40-70°C. A mixture of the three isomers is formed, consisting of 34% o-, 65% p- and 1% m-chloronitrobenzene. Separation is carried out by fractional crystallization and distillation.

The three pure isomers are normally synthesized from the corresponding nitroanilines by the Sandmeyer reaction (Lit.1,23).

p-Chloronitrobenzene is used as a starting compound for the production of azo and sulphur dyes, for the synthesis of fungicides, preservatives, photochemicals and pharmaceuticals.

Larger quantities of chloronitrobenzene, in particular o-chloronitrobenzene, are formed during the production of p-chloronitrobenzene, which is further processed to fungicides. The o- and m-compounds are generally destroyed as waste. Smaller quantities of chloronitrobenzenes are contained in cleaning solutions and distillation residues from the synthesis of compounds which are listed under "use of chloronitrobenzene" (see above).

Waste Treatment

Wastes of high chloronitrobenzene content are currently destroyed in the Federal Republic of Germany on specially equipped incinerator ships at sea. Aqueous wastes with low contents of this poison must be neutralized with lime or undergo a biological pretreatment with activated sludge and subsequent sand filtration before being admitted to the drainage ditch.

Literature:

1. Ullmanns Enzyklopädie der technischen Chemie, 3rd edition, Verlag Chemie Weinheim (1958)
2. Kirk-Othmer Encyclopedia of Chemical Technology, 2nd edition (1964)
3. Beilsteins Handbuch der organischen Chemie, 4th edition, 3rd supplement, Vol. V, Part 2 (609ff)
4. Wagner/Zerlett - Berufskrankheiten der 7. BeKV, Verlag Kohlhammer (1973)
5. Braun, W., Dönhardt, A., Vergiftungsregister, Thieme-Verlag (1970)
6. Moeschlin, B. - Klinik und Therapie der Vergiftungen, Stuttgart (1972)
7. Applegate V.C., Howell J. H., Smith M.A. - Use of mononitrophenols containing halogens as selective sea lamphrey larvicides, Science 127, 336 (1958)
8. Herbert E., Christensen und Thomas T., Luginbyhl The Toxic Substances List 1974, US. Department of Health, Education and Welfare, Rockville, Maryland 20852 (1974)
9. Stiemke, R.E., Eckenfelder, W.W. - A practical method for predicting the effects of common acids and alkalies on the survival of fishes, Bull. 33 Dept. of Eng. Res. N.Car.State Col.; Abs. Sewage Works Journ. 20, 592 (1948)

C ISOCYANATES C

C 1	Toluene Diisocyanate
C 2	Diphenylmethane-4,4-diisocyanate
C 3	
C 4	
C 5	
C 6	
C 7	
C 8	
c 9	
C10	
C11	
C12	
C13	
C14	
C15	
C16	
C17	
C18	
C19	
C20	

Toluene Diisocyanate (TDI)

TOLUENE DIISOCYANATE

Formula $C_9H_6N_2O_2$ $CH_3C_6H_3(NCO)_2$ **CAS no.** 584849

Synonyms tolylene diisocyanate, Desmodur T 65, T 80
Lupranat T 80

Appearance	white to yellowish liquid or solid with pungent odour
Melting point	6 - 21.5°C
Boiling point	251°C
Vapour pressure	0.01 torr at 20°C
Density	1.2 g/cm³
Vapour density ratio (air = 1)	6
Solubility in water	very slightly soluble
Flash point	135°C
Ignition temperature	620°C
Inflammable mixture	0.9 - 9.5 vol. %

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.14	0.14	0.021	0.007				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.007				

Remarks 94<

1 mg/m³ = 0.138 ppm
1 ppm = 7.239 mg/m³

Toluene Diisocyanate (TDI)

TOLUENE DIISOCYANATE

Formula $C_9H_6N_2O_2$ $CH_3C_6H_3(NCO)_2$ **CAS no.** 584849

Synonyms tolylene diisocyanate, Desmodur T 65, T 80
Lupranat T 80

Appearance	white to yellowish liquid or solid with pungent odour
Melting point	6 - 21.5°C
Boiling point	251°C
Vapour pressure	0.01 torr at 20°C
Density	1.2 g/cm^3
Vapour density ratio (air = 1)	6
Solubility in water	very slightly soluble
Flash point	135°C
Ignition temperature	620°C
Inflammable mixture	0.9 - 9.5 vol. %

Toxicity range for short-term exposure:

Man
Warm-blooded animals
Fish
Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.14	0.14	0.021	0.007				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.007				

Remarks 1 mg/m^3 = 0.138 ppm

TOLUENE DIISCOCYANATE

Description of Material

Toluene diisocyanate (TDI) exists in three isomeric forms (2,4-, 2,5-, 2,6- TDI) of which 2,4- and 2,6-TDI normally occur together. Depending on the mixing ratio of the isomers the compound may be present as a colourless to pale yellowish liquid or as a solid. The technical mixture consists of 65% 2,4-TDI and 35% 2,6-TDI. In any case, a sharp pungent odour is characteristic. The toxicity of both forms is qualitatively the same.

Hazards to Man

Toluene diisocyanates are strong irritants. Due to their highly reactive isocyanate groups they attack biochemical structures and lead to tissue necroses, in extreme cases to a "hardening" of tissue. This effect of the liquid compound is limited to the outer skin (mucous membrane) and protects from deeper penetration.

Vapours of the volatile diisocyanates cause strong irritations to the mucous membranes of the eyes and upper respiratory tract in concentrations of only 0.05 to 1 ppm,with accompanying phenomena such as difficulty in breathing, cough, bronchial asthma, which in severe cases may be fatal. Generally, however, no permanent damage will remain, even after severe infliction, except possibly an increased sensitivity. The main source of danger is careless work with so-called DD-lacquers, a mixture of isocyanate (Desmodur) and polyesters (Desmophen), which harden by polymerization after their application (reactive lacquers). During the application of these lacquers a continued fresh air supply, good exhaust system or breathing protection is necessary.

When working in small or poorly ventilated areas, tanks, vessels and other containers, only fresh-air masks should be used. Through a change in the

95<

THN contains only traces of TDI) it was possible to reduce the direct dangers on the job.

In the chemical industry, when working with TDI, attention has to be paid to the fact that TDI sometimes reacts violently with amines, alcohols and acids. During storage and transport, penetration of moisture has to be avoided, since due to the formation of carbon dioxide, the containers may burst.

If TDI burns, highly poisonous nitrogen oxide gases and isocyanate vapours form.

Hazards to the Environment

Toluene diisocyanate reacts with water, forming carbon dioxide (CO_2) and amine (carbamic acid). The amine can react further and form urea.

Poisonous effects on fish and plankton have been described in the literature, but could not be unequivocally interpreted. They may be caused by CO_2, the amine or the urea.

Lethal concentrations for CO_2-containing water are 45 mg/l for trout and 200 mg/l for carp and tench (Lit.1). The corresponding concentrations for amines are 20-60 mg/l and for urea 30-300 mg/l and above (Lit.2).

Experiments with mammals (guinea pigs) showed that repeated inhalation of TDI fog or vapours causes changes in the mucous membranes of the respiratory tract. After moderate damage, regeneration sets in; greater damage leads to purulent inflammation of respiratory tissue ;upon which delayed death is possible (Lit. 3).

After a single four-hour inhalation of 14 ppm (rats, guinea pigs), 12 ppm (rabbits) and 10 ppm (mice) one-half of the tested animals died within two weeks (LC_{50}) (Lit.4). Repeated inhalation (chronic exposure) of 10 ppm TDI 5 x 6 hours caused death in rats within 4-7 days. 1 ppm TDI 10 x 6 hours daily, 6 days per week over 4 weeks could be tolerated by rats without recognizable damage (Lit.5).

Production and Use / Waste Formation

There are numerous ways to synthesize TDI. In Germany the process of phosgenation, that is, the reaction of free diamine with phosgene in o-dichlorobenzene developed by Bayer/Leverkusen, is widely applied (Lit. 6).

The bulk is used for the condensation of TDI with polyfunctional compounds to give high-molecular polyurethane foam. In addition, it is an important constituent in DD-lacquers, adhesives, films and elastomers.

Distillation residues from production are wastes with high TDI contents. Wastes of various concentrations form during production of polyurethane and elastomers (Lit.7).

Waste Treatment

Concentrated wastes from distillation equipment are preferably burnt in special waste incinerators. This also holds for complex and concentrated wastes, which cannot be regenerated by distillation. Because of the high reactivity of TDI, waste waters contain only reaction products from the reaction with water. These can be biodegraded by treatment with activated sludge (Lit. 7).

Literature

1) Münck, F., Stooff, H., Kohlschütter, H., Industrie-Abwässer
Completely revised edition of No. 6 of the series published by the Verein für Wasser-Boden-Lufthygiene Berlin-Dahlem Stuttgart: Gustav Fischer (1968).

2) Patterson, J.W. und Minea, R.A., Wastewater Treatment Technology, 2nd ed., edited by the Illinois Institute of Technology for the Illinois Institute for Environmental Quality, February (1973).

3) Friebel, Luchtrath Dtsch. med. Wschr. 81, 980 (1956).

4) Duncan B., L.D. Scheel, E.J. Fairchild, R. Killens und S. Graham: Amer. Industr. Hyg. Ass. J. 23, 447 (1962).

5) Henschler, D., Assmann, W., und Meyer, K.O.: Arch. Toxikol. 19, 364 (1962).

6) Bayer, O., Angewandte Chemie, edition A 59, 257 (1947).

7) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 Vols., issued for the EPA, TRW System Group, PB 224579, Set/AS 1 February (1973)

Diphenylmethane-4,4-diisocyanate

DIPHENYLMETHANE-4,4-DIISOCYANATE

Formula $C_{15}H_{10}N_2O_2$ $CH_2(C_6H_4NCO)_2$ **CAS no.** 101688

Synonyms 4,4'-diisocyanato-diphenylmethane, MDI, Desmodur 44, p,p-diphenylmethanediisocyanate

Appearance white to pale yellow flakes

Melting point	40 - 41°C
Boiling point	156 - 158°C
Vapour pressure	10^{-5} torr at 25°C
Density	1.18 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	reacts with water
Flush point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	**MAK**	**TLV**	**MIK**		**TA Luft**			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.20	0.20						

Water mg/l	**TwVO**	**PLWS**	**ENV. 140 (EEC)**			**VLWF Group**
			A_1	A_2	A_3	
						S

Remarks

1 mg/m^3 ≙ 0.096 ppm

1 ppm ≙ 1.04 mg/m3

DIISOCYANATES (MDI)

Description of Material

Diphenylmethane-4,4'-diisocyanate (MDI) is a bifunctional aromatic diisocyanate, which at normal temperatures exists as white to pale yellow flakes or as a yellow unstructured solid. It reacts with water to give disubstituted urea, whereby CO_2 evolves.

In general, this compound is known by the following trade names:

Farbenfabriken Bayer :	Desmodur M Desmodur 44
Du Pont :	Hylene M
National Aniline Div.	
Allied Chemicals and Dye Corp.:	Nacconate Type 300

Hazards to Man (Lit.1)

In its effect MDI is similar to tolylene diisocyanate and hexamethyldiisocyanate. It is a strong irritant, affecting in particular the mucous membranes of the respiratory tract. The vapour pressure, however, is so low that toxic concentrations normally cannot form in the breathed air. Dangerous are aerosols which are liberated upon spraying or heating the substance. Within hours after inhaling these fogs complaints occur, such as difficulty in breathing, asthmatic breathing, cough, headaches, pressure on the eyes and loss of the sense of smell. There are occasional indications as to sensitization by MDI. There is proof of the formation of serum antibodies in man after inhalation of 0.13 ppm/30 min.

With proper processing of MDI there will be no damage to health. This is the result of 293 field tests conducted in the refrigerator, automotive, rubber, assembly, construction and steel industries during the years 1965-1971. However, a limit of 0.02 ppm must not be exceeded.

Hazards to the Environment

Inhalation experiments with rats and mice gave the following results:
400 mg/m^3 (40 ppm) inhaled as aerosol by rats and mice over two hours a day caused death in all animals after the second repeat, 150 mg/m^3 (15 ppm) of aerosol over 2 hours a day and eight repeats caused death in 100% of mice and 40% of rats. Lung damage (bronchitis and diffuse pneumonia) was diagnosed as the cause of death (Lit.2).

2 ppm, 5 days a week over 4 weeks were tolerated almost without damage by rats and mice, with only slightly inflamed bronchi and lung parenchyma (Lit.3).

Production and Use / Waste Formation

Production of MDI proceeds mainly by reaction of diphenylmethanediamine with phosgene in a suitable solvent (carbon tetrachloride, chlorobenzenes).
MDI precipitates in crystalline form from the solvent.

MDI is used primarily for the production of polyurethane resins, "Spandex" fibres, for adhesion of rubber to rayon, nylon and similar materials. Besides, it is a constituent of the so-called reactive lacquers (DD-lacquers).

MDI wastes are contained above all in producer effluents and are formed during the production of polyurethane-based polymers (Lit.4).

Waste Treatment

In water MDI is hydrolized to an easily degradable urea derivative. The effluents flow into sewage treatment plants, where a biological secondary treatment follows. Activated charcoal filtration can be added in special cases.

Concentrated wastes are turned over to special waste disposal facilities, since they may contain remainders of phosgene and chlorohydrocarbons from production. Besides, nitrogen oxides are liberated during incineration, so that a scrubber may have to be added (Lit.4).

Literature

1) Henschler, D., Gesundheitsschädliche Arbeitsstoffe, Verlag Chemie 1972/73.

2) Frank, HG.: Zahnmed. Inaugural-Dissertation Würzburg 1964

3) Matheis, G., Zahnmed. Inaugural-Dissertation, Würzburg 19

4) Standford Research Institute, International Umpublished Sources.

D NITRILES

D 1 Acrylonitrile
D 2
D 3
D 4
D 5
D 6
D 7
D 8
D 9
D10
D11
D12
D13
D14
D15
D16
D18
D19
D20

Acrylonitrile

ACRYLONITRILE

Formula C_3H_3N CH_2-CH-CN **CAS no.** 107131

Synonyms vinyl cyanide, propenenitrile,

Appearance colourless liquid with characteristic odour

Melting point	-83.55°C
Boiling point	77.3°C
Vapour pressure	83 torr at 20°C
Density	0.8 g/cm^3
Vapour density ratio (air = 1)	1.83
Solubility in water	soluble (50 g/1 at 20°C)
Flash point	-5°C
Ignition temperature	480°C
Inflammable mixture	3 - 17 %

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	35 - 90 mg/kg
Fish	11 - 100 mg/1
Lower water organisms	20 - 25 mg/1

Occupational safety - Danger symbols F + T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	45	45						I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
		1.99				S

Remarks Danger of resorption through the skin 1 mg/m^3 ≙ 0.44 ppm
1 ppm ≙ 2.25 mg/m^3

ACRYLONITRILE

Description of Material

Acrylonitrile is a colourless liquid of pungent odour resembling that of oil of mustard. However, the odour is detectable only at higher concentrations. The compound is very reactive and tends to polymerize spontaneously. Even irradiation by daylight is sufficient to initiate the reaction and at higher temperatures the reaction may proceed explosively. The pesticides Acrylon and Ventox consist to a large percentage of acrylonitrile.

Hazards to Man

Acrylonitrile is a highly poisonous substance. Its toxicity is based, on the one hand, on the vinyl structure of the molecule, and, on the other, on the nitrile group, which is split off in the organism. Therefore, the poisoning symptoms, with the exception of the irritation to the mucous membranes, correspond to those of hydrogen cyanide poisoning. The weight threshold for acrylonitrile is 4-18 ppm (8-14 mg/m^3), the intolerability threshold above 0.8-1 g/cm^3 (Lit.1). Resorptive poisoning effects (nausea, vomiting, headaches etc.), even at these concentrations may occur, so that the sense of smell fulfills practically only a minor warning function (Lit.2).

Fatal poisonings have seldom been observed in industry. They occurred more often subsequent to the outgassing of rooms with acrylonitrile mixtures for extermination of vermin. The vapours adhere to the gassed object for a long time and can have a lethal effect in spite of subsequent ventilation (Lit.3).

The liquid causes inflammation of the skin after a lengthy latency period and, after prior extended exposure, causes blistering. Also, fatal poisonings are possible as the result of resorption

Hazards to the Environment

The LD_{50} was 50 mg/kg for guinea pigs, 90 mg/kg for rats (Lit.5).

Inhalation experiments gave the following results: Dogs showed weak poisoning phenomena with 40 ppm, the minimum lethal concentration was 110 ppm for 4 hours inhalation. Rats proved less sensitive; the corresponding value after 4 hours inhalation was 600 ppm (Lit.6). In the case of sea fish (perch) 20 mg/1 were harmful. The tolerance level for fresh-water fish was between 38-68 mg/1 (Lit.7,8).

Production and Use / Waste Formation

Today acrylonitrile is produced by the Sohio process from ammonia and a propane/propylene refinery gas mixture. All other processes play a minor role compared to this method.

The bulk of the acrylonitrile produced is used for the production of plastics and synthetic fibres (acrylic fibres, acrylonitrile-butadiene-styrene = ABS plastics, styrene-acrylonitrile = SAN plastics and nitrile rubber) as well as for soil improvement. Furthermore, it forms copolymerization products with vinyl, styrene and similar compounds and is used in the production of other nitriles and the preparation of acryloamide and acrylic acid.

Acrylonitrile wastes are to be expected only in petrochemical plants and the frequently attached polymer production. Due to their quantity they require special disposal provisions (Lit.9).

Waste Treatment

Aqueous wastes with low contents are flushed into the sewerage system and biologically treated in sewage treatment plants. However, it will first have to be determined whether other constituents are present which could interfere with the degradation process. Undegraded remainders can be removed by filtration through activated charcoal.

Concentrated wastes, which are mostly of a very complex nature, are turned over to special waste disposal facilities, if reprocessing appears uneconomical (Lit.9).

Literature

1) Flury, F., et al., Naturforschung und Med. Deutschland Bd. 63 (Pharmakologie und Toxikologie part III, p. 244 (1948)

2) Sartorelli, E. Med. Lav. 57, 184 (1966)

3) Grunske, G. Dtsch.med.Waschr. 74, 1081 (1949)

4) Lorz, H. Dtsch.med.Waschr. 75, 1087 (1950)

5) Ghiringhelli, L. Med. Lav. 45, 305 (1954)

6) Dudley, H.C. J. Ind. Hyg. 24, 27 255 (1942)

7) Henderson, C. et al. The effect of some organic cynides (nitriles on fish). Proc. of the 15th Industrial Waste Conf. 1960 - Engineering Bull. Purdue Univ. 45, 2, 120 (1961)

8) Mckee, J.E. und Wold, H.E. eds., "Water Quality Criteria," 2nd ed., California State Water Resources Control Board, Publication 3 - A 1963

9) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste, issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973

E CYANIDES AND SUBSTANCES WHICH CAN FORM CYANIDES

E 1	Hydrogen Cyanide
E 2	Sodium Cyanide
E 3	Potassium Cyanide
E 4	Calcium Cyanide
E 5	
E 6	
E 7	
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Hydrogen Cyanide

CYANIDES

Formula HCN **CAS no.** 74908

Synonyms hydrocyanic acid

Appearance colourless liquid; odour of bitter almonds

Melting point	-13.4°C
Boiling point	25.7°C
Vapour pressure	600 torr at 20°C
Density	0.687 g/cm³
Vapour density ratio (air = 1)	0.93
Solubility in water	very highly soluble
Flash point	below -20°C
Ignition temperature	535°C
Inflammable mixture	5.4 to 46.6 vol.°/o

Toxicity range for short-term exposure:

Man	1 mg/kg
Warm-blooded animals	4 mg/kg
Fish	0.03 - 0.3 mg/l
Lower water organisms	1 - 16 mg/l

Occupational safety - Danger symbols F + T

Safety guidelines

Air +) mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	10++)	5						

Water +) mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	0.05	0.01+++)	0.05	0.05	0.05	S

Remarks

+) As CN^-

++) Danger of resorption through the skin

1 mg/m³ ≙ 0.890 ppm

1 ppm ≙ 1.123 mg/m³

Sodium Cyanide

CYANIDES

Formula NaCN

CAS no. 14339

Synonyms cyanogran

Appearance	white crystals in powder, flakes, granulated or egg shaped; weak odour of bitter almonds
Melting point	563°C
Boiling point	1496°C
Vapour pressure	1 torr at 817°C
Density	1.60 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	highly soluble (30 wt %
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	<5 mg/kg
Warm-blooded animals	
Fish	0.05 - 5 mg/l
Lower water organisms	3.4 mg/l

Occupational safety - Danger symbols

Safety guidelines

Air +) mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
	$5^{++)}$	5						

Water +) mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A$_1$	A$_2$	A$_3$	
	0.05	0.01	0.05	0.05	0.05	

Remarks +) As CN$^-$

++) Danger of resorption through the skin ! On contact with

Potassium Cyanide

CYANIDES

Formula KCN-

CAS no. 151508

Synonyms

Appearance	white crystals as powder, flakes or granulated; weak odour of bitter almonds
Melting point	635°C
Boiling point	
Vapour pressure	
Density	1.52 g/cm³
Vapour density ratio (air = 1)	
Solubility in water	very highly soluble
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	< 5 mg/kg
Warm-blooded animals	1.6 - 15 mg/kg
Fish	0.4 - 3 mg/l
Lower water organisms	0.4 - 40 mg/l

Occupational safety - Danger symbols

Safety guidelines

Air +) mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	5++)	5						

Water +) mg/l	TWVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	0.05	0.01	0.05	0.05	0.05	

Remarks +) As CN^-

++) On contact with moisture or acidic water poisonous

Calcium Cyanide

Formula $Ca(CN)_2$

CAS no. 592018

Synonyms

Appearance white powder or colourless rhombohedral crystals

Melting point decomposes at > 350°C

Boiling point

Vapour pressure

Density

Vapour density ratio (air = 1)

Solubility in water highly soluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man < 5 mg/kg

Warm-blooded animals

Fish 0.05 - 0.5 mg/l

Lower water organisms 0.01 - 3.4 mg/l

Occupational safety - Danger symbols

Safety guidelines

Air +) mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	5++)	5						

Water +) mg/l	TwVO	PLWS	ENV. 140 (EEC).			VLWF Group
			A_1	A_2	A_3	
	0.05	0.01	0.05	0.05	0.05	

Remarks +) As CN^-

++) Danger of resorption through the skin. On contact with moisture or acidic water or acids the poisonous hydrogen cyanide

CYANIDES

Description of Material

Cyanides are salts of

Hydrocyanic Acid

Hydrocyanic acid is a colourless liquid which is miscible with water in all proportions and is weakly acidic in aqueous solutions. If not stabilized (e.g. by addition of oxalic acid or sulphur dioxide) hydrocyanic acid tends to polymerize spontaneously upon heating. Pure hydrocyanic acid evaporates very quickly and gives off the characteristic odour of bitter almonds.

Sodium Cyanide

This substance crystallizes in cubes and is normally available as white powder, which is highly soluble in water. Due to hydrolysis the aqueous solution is strongly alkaline.

Potassium Cyanide

Potassium cyanide is hygroscopic and therefore forms in air coarse-grained or lumpy white salts. Due to hydrolysis the aqueous solution is strongly alkaline and smells like hydrocyanic acid. After standing some time or during evaporation the solution decomposes to ammonia and potassium formate.

Calcium Cyanide

This white powder decomposes slowly in moist air, giving off hydrocyanic acid. Calcium cyanide is highly soluble in water, with gradual liberation of hydrocyanic acid.

Barium Cyanide

Barium cyanide is a water-soluble, white, crystalline powder (CAS No. 542621).

CYANIDES

Nickel Cyanide

Nickel cyanide is a light green powder, which is virtually insoluble in water. It reacts, however, with dissolved alkali and alkaline earth cyanides to form soluble tetracyano nickel salts (CAS No. 557197).

Silver Cyanide

Silver cyanide is a white, odourless and tasteless powder. On exposure to light it slowly colours brown, with precipitation of silver. Silver cyanide is virtually insoluble in water (CAS No. 506649).

The cyanides discussed are the most important within the group of the so-called normal cyanides. In addition to this group many complex cyanides are known. These complex compounds are not nearly as poisonous as the normal cyanides; cyanide ions can only be detected after destroying the complex.

Hazards to Man

The average lethal dose of soluble cyanide ions in man is 50 to 60 mg for oral intake. From lethal poisonings upon a single intake, a minimum lethal dose of 0.7 mg/kg body weight was concluded (Lit.1). It is reported in the technical literature that 2.9 to 4.7 mg cyanide ions per day are harmless (Lit.2). In their physiological effect, volatile cyanides are similar to hydrocyanic acid. By impeding tissue respiration and paralyzing the respiratory centre they can cause death by "internal suffocation".

Daily exposure of the skin to a cyanide solution can lead to "cyanide rash", characterized by itching and formation of spots, papules and blisters. Even in low concentrations, cyanide can be resorbed through the skin.

Long-term intake of small amounts may lead to loss of appetite, headaches, weakness, nausea and dizziness. Upon intake of vapours and dusts, irritation or inflammation of the eyes and upper respiratory tract occur as additional symptoms.

Hazards to the Environment

Even low concentrations of hydrocyanic acid or soluble cyanides harm the biocoenosis of waters. Fish show a particularly high sensitivity. The lethal cyanide concentration for trout is only 0.05 mg/1 (Lit.3). The lethal concentrations for other fish are mostly somewhat higher. For lower water organisms the toxic effect begins at 0.01 mg/1. Within this group of organisms the lethal concentration for small crustaceans (Daphnia) has been determined as 3.4 mg/1, for algae 40 mg/1 (Lit.4,5,6).

The lethal doses for domestic animals are according to literature data 40 mg for dogs and sheep and 390 mg for cows and horses (Lit. 7).

Production and Use / Waste Formation

Hydrogen Cyanide (Hydrocyanic Acid)

There are various processes for producing hydrogen cyanide on a large scale. Several methods have been developed for the catalytic reaction of ammonia and methane (or natural gas) at temperatures in the range of 1000-1400°C; these operate either with addition of air (e.g. Andrussow process) or without addition of oxygen (e.g. Degussa process). The catalytic reaction of carbon monoxide and ammonia to hydrogen cyanide and water proceeds at 700°C. Newer methods use carbon powder, whereby, however, only 75% of the ammonia are converted to hydrogen cyanide. Hydrocyanic acid may also be produced from coke-oven gas and by pyrolytic decomposition of sugar beet molasses.

CYANIDES

Hydrocyanic acid is used for pest control in closed areas (e.g. hot houses, mills, silos). In this application (trade name: Cyclon) it is mixed with the strong smelling methyl chlorocarbonate (as a warning indicator!) and is sold in containers with highly absorbing materials (diatomaceous earth or cellulose). Hydrocyanic acid is of increasing interest as an intermediate for the production of important monomers (e.g. acrylonitrile, methyl methacrylate, adiponitrile, chlorocyanuric acid), for the manufacture of synthetic fibres, transparent polymers and copolymers. Hydrocyanic acid is furthermore an intermediate in the production of cyanides, dyes and chelating agents.

Hydrocyanic acid occurs in waste gases and waste waters of producing and processing plants. Other hydrocyanic acid emitters are coking plants, gas plants, petroleum refineries and plants working with cyanides.

Cyanides

Today alkali cyanides are technically produced mostly by neutralization of hydrocyanic acid with potassium or sodium hydroxide. Other manufacturing processes are based on the reaction of carbon monoxide and ammonia with soda and potash at about 600°C or on the reaction of a mixture of alkali salts and nitrogen-containing carbon (from blood, horn etc.) at about 800°C. An important process for the production of cyanides is preparation of calcium cyanamides by azotizing calcium carbide. The reaction of calcium carbide with nitrogen takes place above 1000°C in a highly exothermic reaction with calcium cyanide as an intermediate. Sodium cyanide can be prepared from the reaction product, calcium cyanamide, e.g. by melting with rock salt or so-called "black cyanide", a mixture of sodium and calcium cyanide with carbon impurities. Alkali cyanides in turn are starting materials for the preparation of other cyanides.

CYANIDES

Cyanides are frequently intermediates in the synthesis of synthetic fibres, pharmaceuticals, dyes and pesticides. Large quantities of cyanides are used for surface finishing of metals. One method is a heat treatment of steel and other ferrous materials and is known as salt bath hardening. In another method cyanides are used for electrochemical surface treatment of materials (galvanizing), particularly in electroplating. Cyanide hardening salts are mainly sodium and potassium compounds. A further area of application of alkali and alkaline earth cyanides is the dressing of ores. In cyanide leaching, silver- and gold-containing ores are treated, after crushing, with solutions of potassium or sodium cyanide, which dissolve the noble metals and their compounds as complex cyanides. From this solution (leach) gold is precipitated by the addition of zinc chips, silver by electrolysis or by addition of zinc. Black cyanide (mixture of sodium and calcium cyanide) is also used as a so-called inhibitor during the flotation of lead/zinc, copper and other sulphidic ores.

Cyanide-containing effluents and sludges are formed primarily during electroplating (electrodeposition), e.g. copper plating, zinc plating, brass plating, nickel plating, cadmium plating and silver plating. In addition to these so-called electroplating concentrates and semi-concentrates (e.g. rinse and wash water), spent cyanide-containing baths may be formed during the surface treatment of materials when degreasing and pickling (derusting, descaling). A typical liquid waste concentrate from electroplating of metals with copper contains copper alkali cyanide, sodium cyanide, sodium sulphonate, hydrocarbons and zinc phosphate. Liquid wastes from zinc plating contain cyanides of zinc, nickel and silver in a sodium hydroxide solution. Due to the high solubility of cyanides the cyanide content of electroplating sludges is found mainly in the salt bath hardening shops. In cyanide-containing hardening salt wastes the distinction has to be made between:

- carburizing bath wastes

For the regeneration or a change in composition a part of the carburizing bath has to be discarded. These wastes contain alkali cyanide (3-40%) and alkali cyanate (2-45%) in addition to various amounts of barium chloride and carbonate and alkali chloride and carbonate.

- nitriding bath wastes

Spent nitriding baths or melt discharges contain mostly high concentrations of alkali cyanide (3-40%) or alkali cyanate (2-45%)in addition to alkali carbonate formed by oxidation.

- hot quenching bath wastes (from tempering salt baths)

Melts from cyanide-containing hardening baths are introduced by nitrided or carburized metal parts into the tempering baths, which consist mainly of alkali nitrites and nitrates. During removal of the sludge, which collects in the lower third of the baths, hydroxides, chlorides, carbonates of sodium, potassium and barium together with considerable amounts of attached base melt (cyanide salts!) are obtained.

- oil bath wastes

If metal parts are quenched in oil after a carburization treatment, a mixture of salts of alkali cyanide and chloride and barium chloride and carbonate collects at the bottom of the oil bath.

CYANIDES

Waste Treatment

Several methods are available for the detoxication of aqueous solutions of hydrocyanic acid or cyanides. The cyanide concentration and the presence of other impurities determine the choice of the treatment. Effluents with relatively low amounts of cyanides are detoxicated best by oxidation with hydrogen peroxide or ozone. Catalytic oxidation using the BUCKSTEEG method is not always applicable due to the poisoning of the carbon catalyst by ferric and ferrous cyanide.

Concentrated cyanide solutions can be treated in an oxidation process with elemental chlorine or sodium hypochlorite solution (commercially available with 13-15% active chlorine). The detoxication progresses in several reaction steps through the formation of cyanogen chloride and cyanate to the possible end products ammonia, hydrogen carbonate or carbon dioxide and nitrogen (only with a surplus of oxidizing agent). The formation of cyanate proceeds sufficiently fast only at higher pH values (pH 10-11). A 30% solution of sodium hydroxide is most suitable to make the solution alkaline. For the oxidation of 1 kg cyanide to cyanate about 10 kg of commercial hypochlorite solution are needed; the oxidation to carbon dioxide and nitrogen requires about 25 kg (Lit. 8). For reasons of safety, care has to be taken that during the reaction the temperature of the liquid concentrate does not exceed 38°C, because otherwise the initially formed cyanogen chloride escapes. Cyanogen chloride is a strong poison. It is easily detectable, since even small amounts in the air cause heavy tearing of the eyes.

A detoxication of concentrated cyanide solutions takes place to a certain degree by the transformation of cyanides into less toxic complex salts, such as ferrous and ferric cyanides (e.g. Prussian blue).

CYANIDES

Upon addition of sufficient amounts of ferrous sulphate to the cyanide-containing solution, the complex salts are precipitated and may be discarded as sludge. The advantage of this method is its comparative simplicity at low cost. The disposal of the complex salts, however, is not without problems, because upon irradiation with light they can decompose,with liberation of hydrocyanic acid.

A further method for the treatment of cyanide concentrates is based on the incineration of hydrocyanic acid, which is liberated from aqueous cyanide solutions by the addition of acids (known as: Cyan-Kat process). The process is rather intricate and requires in addition to extensive safety measures a continuous mode of operation. This is also true of the process proposed by SCHINDEWOLF (Lit.9) involving hydrolysis and saponification of aqueous cyanide solutions at 150-200°C. The final products of this method are alkali formate and ammonia, which require further treatment. Another method of treating cyanide-containing concentrates, which appears technologically promising but is relatively cost-intensive, is the electrolytic decomposition of cyanides.

In the Federal Republic of Germany solid cyanide wastes (e.g. from salt bath hardening) are currently disposed of in underground dumps (salt mine of Kali and Salz AG, 6251 Herfa-Neurode). During transport and deposit the wastes have to be packaged in sealed steel drums.

Future alternatives to this form of dumping of salt hardening wastes are offered by two processes, for which patents have recently been applied (Goldschmidt AG/Degussa). They are based on the reaction of the cyanide/cyanate portion of the wastes with their nitrite/nitrate content (Lit.10,11,12). In this reaction the cyanide compounds are oxidized to

CYANIDES

Literature

1) Halstrom, G. und Moller, K.O.
Acta pharmacol. (kbh) I, 18 (1945)

2) Mckee, J.E. und Wolf, H.E. (editors)
Water Quality Criteria (2nd edition)
California State Water Resources Control Board
Publication 3 - A 1963

3) Karsten, A.
Effect of Cyanide on Black Hills Tront
Black Hills Eng. 22, 145 (1934), J.A.W.W.A 28, 660 (1036)

4) Anderson, B.G.
Sewage Works J. 16, 1156 (1944), 18, 82 - 87 (1946)

5) Banrick, H.F. und Muller, F.M.
J. Microbid. Serol. Antonie van Leeuwenhoek 17, 171 (1951)

6) Marsson, M. und Weldert, R.
Mitt. Königl. Landesanst. Wasserhyg. 22, 237 (1917)

7) Mckee, J.E. und Wolf, H.E. (editors)
Water Quality Criteria (2nd edition)
California State Water Resources Control Board
Publication 3 - A 1963

8) Hartinger, L.
Abwasserreinigung in der Galvanotechnik
Umweltschutz-Städtereinigung No. 11 / 1971,
Nos. 2 & 3 / 1973

9) Hoerth, J., Schindewolf, U. und Zbinden, W.
Entgiftung von Cyanid-Abfällen durch Verseifung
Chemie-Ingenieur-Technik 1973 / No. 10a

10) Müller, W. und Witzke, L.
Die Entgiftung und Aufarbeitung aller in Salzhärtereien anfallenden Abfälle
Chemie-Ingenieur-Technik 1973 / No. 22

11) Beyer, H., Dittrich, G., Kunst, H. und Schmidt, F.
Neuere Entwicklungen in der Wärmebehandlung von Metallen in Salzbad. Ein Beitrag zum Umweltschutz
Chemie-Anlagen und Verfahren 1973, No. 11

12) Materialien zum Abfallwirtschaftsprogramm 1975 der Bundesregierung (in preparation).

F

POLYCYCLIC HYDROCARBONS, INCLUDING CONDENSED SYSTEMS

F

F 1
F 2
F 3
F 4
F 5
F 6
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G PHENOLS AND THEIR DERIVATIVES G

G 1	Phenol
G 2	Cresol
G 3	Benzoquinone
G 4	Pentachlorophenol
G 5	
G 6	
G 7	
G 8	
G 9	
G10	
G11	
G12	
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G20	

Phenol

PHENOL

Formula C_6H_6O C_6H_5OH **CAS no.** 108952

Synonyms hydroxybenzene, carbolic acid, oxybenzene, phenyl hydroxide

Appearance colourless to reddish crystals, very hygroscopic

Melting point	41°C
Boiling point	182°C
Vapour pressure	0.35 torr at 25°C
Density	1.07 g/cm^3
Vapour density ratio (air = 1)	3.24
Solubility in water	soluble (67 g/l at 20°C)
Flash point	79°C
Ignition temperature	605°C
Inflammable mixture	varies

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	0.42 - 1.3 g/kg
Fish	1 - 63 mg/l
Lower water organisms	7 - 100 mg/l

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	19	19	0.6	0.2				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.001	0.001	0.005	0.1	S

Remarks Danger of resorption through the skin

1 mg/m^3 ≙ 0.265 ppm
1 ppm ≙ 3.8 mg/m^3

PHENOL

Description of Material

Pure phenol forms colourless, peculiarly smelling needles, which turn reddish in air and deliquesce.

Small amounts of moisture lower the melting point considerably; phenol with 2% water melts at 33°C. The aqueous solution of phenol is weakly acidic. With alkalis, phenol forms salts, the phenolates. In practice phenol is used either in its dry crystalline state or as a 10% solution (carbolic acid) or 1.3% solution (carbolic water).

Hazards to Man

Phenol is used under the names of carbolic acid and carbolic water for disinfecting rooms, tools, etc. In the past it was even used for disinfecting wounds. Today it is known with certainty that phenol is a strong physiological poison. It burns the skin and is easily resorbed. Initially, the affected area of the skin is sore, later becomes insensitive, but continues resorbing and colours in succession white, red and brown. With concentrated solutions or deep penetration, damage to vessels is possible (phenolic gangrene). Resorption through the skin can even lead to fatal poisonings. Burns on the cornea lead to permanent impairment of vision due to formation of scars. Upon oral intake of carbolic acid, mucous membranes in the mouth, oesophagus and stomach are severely burnt.

Resorption effects manifest themselves in numbness, dizziness and buzzing in the ears, increased salivation and increasingly by disorders of the circulatory and nervous systems, which lead to unconsciousness. After intake of a lethal dose - orally 10-15 g - or on inhalation of concentrated vapours, death can occur within a short time through respiratory paralysis or severe collapse.

PHENOL

Delayed damage has been observed in disorders of the kidney and liver functions, change in the blood count and inflammation of the bronchi.

Hazards to the Environment

The poisonous effect on fish and plankton has been proven. The danger threshold for fish is 10 mg/1 (Lit.1), for algae (Scenedesmus) 40 mg/1 and for small crustaceans (Daphnia) 16 mg/1 (Lit.2).

Long-term exposure increases sensitivity to phenol and leads to a decrease in the danger threshold. LC_{50} values for an observation period of up to 90 hours for fish are between 1 and 20 mg/1 at 20°C (Lit.3).

Phenol concentrations of 0.1 - 0.2 mg/1 affect the taste of edible fish. Plant cultures which had been watered with phenol-containing water, did not show any damage (Lit.4). Certain species of rush have been reported to take up phenol and thus contribute to the self-cleaning of waters (Lit.5). Also, yeast may be utilized to degrade phenol (Lit. 6).

Production and Use / Waste Formation

Up to about 1950 phenol was produced from the middle fraction of coal tar that distills between 170° and 250°C and from coking plant waste waters.

Due to the increasing manufacture of synthetic resins the production of phenol by this method was insufficient, so that today the bulk is synthesized.

Four processes have gained practical importance:

1. Sulphonization of benzene to benzenesulphonic acid
2. Chlorination of benzene to chlorobenzene

3. Hock cleavage
   Oxidation of cumene by atmospheric oxygen to cumene hydroperoxide, which is cleaved by acid to phenol and acetone.
4. Dow process
   Oxidation of toluene to phenol and benzoic acid.

Phenol is used in the chemical industry for the production of synthetic resins (phenol-formaldehyde condensation products, phenolic resins), dyes, pharmaceuticals, pesticides, plasticizers, synthetic tanning agents, fragrances, picric acid, biphenol, lubricants and numerous other chemicals as well as solvents.

Various quantities of phenol-containing effluents are produced during the preparation of the following, primarily petrochemical products:

Phenol, cumene, ethylene, propylene, phenylglycine, naphthalene, butadiene, acrylonitrile, detergents, synthetic resins, cresol, substituted cresols, dicumylperoxide, acetylene, benzene, toluene (Lit.7).

Considerable amounts of phenolic wastes are formed in petroleum refineries by processes such as fractionation, catalytic cracking, drying and desulphurizing of mineral oils, isomerization of butane and naphthenes (Lit.8).

Waste Treatment

The most important method, equally applied by refineries and petrochemical plants, is the biodegradation of phenol (activated sludge basins, aeration ponds, trickling filters). With this a 65-99% degradation of phenol is attained. A further decrease (80-90%) of the phenol content is obtained by treatment with ozone or activated charcoal (Lit.9).

PHENOL

Literature

1) Steinmann, P., Surbeck, G.,: Die Wirkung organischer Verunreinigungen auf die Fauna schweizerischer fließender Gewässer. Preisausschreiben der Schweiz Zool. Ges., Bern 1918

2) Bringmann, G., Kühn, R.: Vergleichende wassertoxikologische Untersuchungen an Bakterien, Algen und Kleinkrebsen. Gesundh. Ing. 80, 115 - 119 (1959)

3) Capener, E. rt al.: Entwurf eines Handbuches über gefährliche Abfälle, Research Institure Menlo Park, California, on behalf of the BMI (1974)

4) "Oil and Hazardous Materials, Emergency Procedures in the Water Environment", Report No. CWR 10-1, U.S. Department of Interior, Federal Water Pollution Control Administration, October 1968

5) Seidel Naturwissenschaften 50 (1963) 452 ff. und 52 (1965) ff

6) Chemiker Ztg. 90 (1966) 203 - 207

7) Gloyna, E.F. et al.: "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes" Federal Water Pollution Control Administration 1970

8) Gloyna, E.F. et al.: "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes", Federal Water Pollution Control Administration 1970

9) "The Cost of Clean Water" Vol. III Industrial Work Profiles, No. 5 - Petroleum Refining, U.S. Department of Interior, Federal Water Pollution Control Administration 1967.

Cresol

CRESOL

Formula C_7H_8O $C_6H_4(CH_3)OH$ **CAS no.** 95487 (o-)

Synonyms methylphenol, hydroxytoluene, cresylic acid

Appearance colourless to dark brown liquid

Melting point	12 - 35°C
Boiling point	192-201°C
Vapour pressure	1.7 - 3.5 torr at 60°C
Density	1.03 - 1.05 g/m³
Vapour density ratio (air = 1)	3.72
Solubility in water	soluble (20 g/l at 20°C)
Flash point	43 - 82°C
Ignition temperature	555 - 645°C
Inflammable mixture	>1.1 vol.°/o

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	
Fish	3 - 15 mg/l
Lower water organisms	10 - 100 mg/l

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	22	22						I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.001				S

Remarks The data refer to the isomer mixture
1 mg/m³ ≙ 0.23 ppm
1 ppm ≙ 4.4 mg/m³
CAS-Nr. : 108349 (m-cresol), 106465 (p-cresol)

CRESOL

Description of Material

Cresol is a liquid of phenolic odour and, depending on age, duration of exposure to light and degree of purity, can be colourless to dark brown. Due to its chemical structure three isomeric forms have to be distinguished: ortho-, meta-, para-cresol. All three forms are present in coal tar. They are isolated as the isomeric mixture and are generally applied in industry without further separation. A cresol-containing detergent solution is used as a disinfectant under the name of "Lysol".

Hazards to Man

The effects of cresol resemble to a lesser degree those of phenol. Cresol causes bad chemical burns on the skin and mucous membranes. The compound is resorbed through the intact skin. The affected area of the skin becomes, after initial pains, insensitive, but continues resorbing and colours in succession white, red and brown. With concentrated solutions or upon deep penetration, damage to vessels and lethal effects are possible. Poisonings by oral intake can cause severe disorders of the gastrointestinal tract, combined with liver and kidney damage, and less frequently disorders of the central nervous system. Damage to the cornea heals always with the formation of bad scars and leads to an impairment of vision.

Cresol belongs to the combustible liquids which require special precautions. Rooms where cresol is being worked with have to be equipped with an adequate exhaust system for the evolving vapours. Personnel has to wear protective clothing and, especially, safety goggles.

CRESOL

Hazards to the Environment

An aqueous solution of cresol represents a poisonous, burning liquid, even in a dilution of 1 : 50. The toxicity of cresol to fish (3-15 mg/l) seems to depend on the oxygen concentration of the water; a low oxygen content enhances the effect (Lit.1). Cresol contents below 3 mg/l over a longer exposure period lead to changes in the taste of fish (storage in fatty tissue).

Production and Use / Waste Formation

Cresol is prepared industrially - among other methods - from carbolic oil, which is separated at 170-230°C during distillation of coal tar. The "phenolate liquor" is separated by extraction with sodium hydroxide solution or, in the Phenoraffin process of Lurgi, with aqueous sodium phenolate solution and isopropyl ether. Ortho-cresol is obtained by rectification of "crude phenol", meta- and para-cresol by formation of adducts, e.g. with benzidine and urea. Also, during the processing of petroleum, cresols are formed during cracking. However, since during these processes other products are obtained with higher yields, the cresol-containing fractions are normally discarded into the waste-water systems of these plants. If it is considered economical, the cresols are today extracted with sodium hydroxide. Cresols are used as a raw material for the production of cresolic resins, which are prepared by condensation of cresol mixtures with formaldehyde; as solvents for the manufacture of wire coatings; in the form of their phosphoric acid esters as hydraulic fluids; as a disinfectant; as a synthetic tanning agent; as a base material for the production of tricresyl phosphate; as a plasticizer for PVC plastics; for the preparation of various dyestuffs, pesticides and antioxidants. Cresols are moreover constituents of anti-foaming agents and are used as stabilizing agents in electrolytic cells. Cresols are also applied in wet ore dressing (flotation).

In addition to the mentioned methods of production and processing, various quantities of cresol wastes are produced: by gas plants, which use coal for the manufacture of synthesis gas, by wood distillation, by coking plants and processing installations for coal mines, by synthetic-resin producers, by chemical plants that produce cresol as an intermediate, and by the application of disinfectant solutions in large animal farms (Lit.1).

Waste Treatment

Waste waters with medium cresol contents (5-50 mg/1) may be subjected to a biological treatment (oxidation ponds, trickling filters, activated sludge basins). In this way it is possible to reduce the cresol content to 1-0.5 mg/1. In order to lower the content still further, chemical or physicochemical treatment methods are required (treatment with activated charcoal, ozone). With ozone the content of biologically pretreated refinery effluents can be reduced from 0.35-0.16 mg/1 to 0.003 mg/1 (Lit.2).

Cresol wastes of high concentration are destroyed in special waste incinerators.

Literature

1) Mckee, J.E. und Wolf, H.E.
"Water Quality Criteria", 2nd ed.,
California State Water Resources Control Board,
Publication 3 - A 1963

2) Ottinger, R.S. et al.,
"Recommended Methods of Reduction, Neutralization,
Recovery or Disposal of Hazardous Waste",
TRW Systems Group, PB 224579, Set/AS
1 February 1973

Benzoquinone

BENZOQUINONE

Formula $C_6H_4O_2$ OC_6H_4O **CAS no.** 106514

Synonyms quinone, p-quinone

Appearance golden-yellow, pungent smelling crystals

Melting point	116°C (sublimes)
Boiling point	
Vapour pressure	
Density	1.08 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	slightly soluble (14 g/l at 24°)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	130 mg/kg
Fish	0.1 - 10 mg/l
Lower water organisms	0.4 mg/l

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.4	0.4						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.2				

Remarks

1 mg/m^3 ≙ 0.25 ppm
1 ppm ≙ 4 mg/m3

BENZOQUINONE

Description of Material

Benzoquinone exists in two isomeric forms, 1,2-and 1,4-benzoquinone, of which only the 1,4-compound is of practical importance. It forms golden-yellow, pungent smelling crystallites (prisms), which sublime very easily and are volatile with steam. They are highly soluble in organic solvents such as alcohol, ether and hot ligroin, but slightly soluble in water. The compound is very reactive. Characteristic is its ease of reducibility to hydroquinone. During reduction quinhydrone is formed, a 1:1 addition compound of quinone and hydroquinone.

Hazards to Man

At a sufficient concentration and after extended exposure benzoquinone causes irritations to the skin and mucous membranes. In particular, damage to the cornea has been noted (acknowledged occupational disease). Initially, the irritation effects of benzoquinone are unspecific. After extended exposure of several years, a characteristic yellow-brown discoloration in the region of the eyelid margin appears. Then, fine to larger clouds develop in the corneal epithelium and parenchyma. The cornea may swell and deform, which may lead to an irregular astigmatism, which cannot be completely corrected. The ability for regeneration is generally reduced. Frequently an increased susceptibility to secondary infections remains. Permanent damage to the eyes, such as turbidity, astigmatism, deformations, were frequently observed, in some cases even loss of vision (Lit.1).

All open working methods in which quantities of benzoquinone are taken up by the moisture of the air or are distributed by dust are dangerous.

The olfactory threshold is 0.1 ppm; even 0.5 ppm are strongly irritating. To safeguard against damage, wearing of airtight safety goggles is indispensable.

BENZOQUINONE

Hazards to the Environment

130 mg/kg are toxic to warm-blooded animals. Lethal concentrations for fish vary between 0.1 and 10 mg/l. A content of 0.5 mg/l affects the taste of edible fish (Lit. 2).

Production and Use / Waste Formation

Industrial production starts with aniline, which is oxidized with manganese dioxide (MnO_2) or chromic acid and sulphuric acid to 1,4-benzoquinone (Lit.3).

1,4-Benzoquinone is mainly a starting material for hydroquinone. To a smaller extent it is also an intermediate for dyes (indole dyes, mordant dyes), vitamins (K,E), bactericides (Iversal, Ambozal), insecticides and fungicides (chloranil). Hydroquinone is a significant component of photographic developers, is utilized as a tanning agent and serves as an inhibitor for undesired polymerization reactions.

All listed methods for the production and processing of quinone and hydroquinone contribute to the formation of quinone wastes, which, however, burden primarily the effluents (Lit. 4).

Waste Treatment

Diluted waste waters may be purified by biological means with specially adjusted activated sludge. Biodegradation is greatly facilitated if the quinone wastes are reduced to hydroquinone prior to discharge. Suitable reducing agents are sodium sulphite and sulphur dioxide.

Concentrated wastes are disposed of in special waste incinerators, whereby attention has to be given to the fact that quinone sublimes (Lit. 4).

BENZOQUINONE

Literature

1) Valentin, H. et al.: Arbeitsmedizin, Thieme Verlag 1971.

2) McKee, J.E. und Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963

3) Fiat Final Report 1313 D.S. 164. Quoted in: Ullmann Enzyklopädie der Technischen Chemie, 4th edition (1975), Verlag Chemie/Weinheim.

4) Ottinger, R.S. et al.: "Recommended Methods of Reduction, Neutralization, Recovery of Disposal of Hazardous Waste", 16 vols., issued for the EPA, TRW Systems Group, PB 224 579, Set/AS 1 February 1973.

Pentachlorophenol

PENTACHLOROPHENOL

Formula C_6HCl_5O C_6Cl_5OH **CAS no.** 87865

Synonyms Penta

Appearance white, needle-like crystals, pungent odour

Melting point 190°C

Boiling point 310°C

Vapour pressure

Density 1.98 g/cm^3

Vapour density ratio (air = 1)

Solubility in water virtually insoluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	70 - 550 mg/kg
Fish	0.2 - 1 mg/l
Lower water organisms	10 mg/l (snails)

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.5	0.5						

Water mg/l	TWVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
						S

Remarks Danger of resorption through the skin

1mg/m^3 $\hat{=}$ 0.1 ppm

1 ppm $\hat{=}$ 10 mg/m^3

PENTACHLOROPHENOL

Description of Material

Pentachlorophenol belongs to the group of chlorinated phenols which play a role as pesticides. Pure pentachlorophenol consists of white, needle-like crystals, which are stable in air and have a weak but pungent odour.

It is almost insoluble in water, but soluble in a sodium carbonate solution, because it is converted to the sodium salt (phenolate). The solubility of Na-pentachlorophenolate in water is 224 g/l at 20°C.

Hazards to Man

Similar to phenols, pentachlorophenol degenerates tissue severely. Vapours and dusts cause bad irritations of the skin and mucous membranes. The cornea is especially endangered. Repeated and continued contact with the solid as well as with salt solutions lead to burns on the skin.

The greater danger lies in the fact that toxic to lethal doses can get into the body via resorption through the skin, especially when working with phenolate solutions. Similar to dinitrophenol, pentachlorophenol affects the metabolism of the cell as an initiator of oxidation and phosphorylation processes and leads to a great increase in the basal metabolic rate. Poisoning is accompanied by headaches, nausea, vomiting, stomachache, angina, rise in temperature to 40°C and above, accelerated breathing, muscular weakness, cramps. In severe cases, death results from circulatory failure and respiratory paralysis. The lethal dose is considered to be 30 mg/kg (Lit.1).

Chronic poisonings are possible too and lead to liver and kidney damage, loss of weight, heavy perspiration, acne and furunculosis.

PENTACHLOROPHENOL

Hazards to the Environment

Pentachlorophenol acts as a poison on higher as well as lower organisms. 25 mg per kg and day of pentachlorophenol are toxic to cattle and sheep; 100-200 mg/kg are an acute lethal dose (Lit.2).

Snails are destroyed by concentrations of 2.5 to 10 mg/l (Lit.3).

0.2-1.0 mg/l cause death in fish; 0.1 mg/l is considered a harmless concentration.

For eradication of the water hyacinth, a concentration of 80 mg/l is required (Lit.3). It was detected in plant cells that pentachlorophenol has mutagenic effects (Lit.4).

Production and Use / Waste Formation

Pentachlorophenol is produced on a technical scale by the hydrolysis of hexachlorobenzene with concentrated aqueous or alcoholic sodium hydroxide or by chlorination of phenol in the presence of activated charcoal or tertiary bases such as pyridine, quinoline and others.

It is commercially available under the names Preventol P, Dowicide 7, Santophen 20, Cryptogil OL; the sodium salt under the names Preventol PN, Dowicide G, Santobrite, Cryptogil Na.

Pentachlorophenol is used above all in pest control. It is applied as a herbicide on pineapple and sugar cane plantations, as an algae control agent and fungicide in protective coatings, as a bactericide, molluskicide and wood preservative against fungi and wood-attacking insects (termites). In its last mentioned function it is applied to the wood as the highly soluble sodium salt and reconverted inside the impregnated wood to pentachlorophenol by a posttreatment with acid or carbon dioxide gassing.

PENTACHLOROPHENOL

Wastes of pentachlorophenol are formed mainly during production of the substance, but its application as a pesticide also gives rise to considerable quantities of pentachlorophenol wastes as residual solutions or batches that turned useless.

Waste Treatment

Before draining, aqueous solutions of low concentration must be purified of the poisonous pentachlorophenol by filtering methods such as adsorption of the harmful material by activated charcoal. After this step, the charcoal is regenerated by controlled oxidation in a rotary kiln incineration installation. The escaping hydrogen chloride gas is removed from the flue gas by scrubbers.

Concentrated wastes are destroyed in special waste incinerators which have suitable installations to scrub the liberated hydrogen chloride gas (Lit.5).

Literature

1) The Toxic Substances List, 1973 ed., U.S. Department of Health Education and Welfare, June 1973.

2) Hapke, H.J. Toxikologie für Veterinärmediziner, F. Enke-Verlag Stuttgart 1975.

3) McKee, J.E. und Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

4) "Water Quality Criteria Data Book" Vol. 1, Organic Chemical Pollution of Freshwater, EPA Report No. 18010 DPV 12/70, A.D. Little, Inc. December 1973.

5) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 Vols., issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1. February 1973.

H SOLVENTS WITHOUT ORGANOHALOGEN COMPOUNDS

H 1	Xylene
H 2	Benzene
H 3	Toluene
H 4	
H 5	
H 6	
H 7	
H 8	
H 9	
H10	
H11	
H12	
H13	
H14	
H15	
H16	
H17	
H18	
H18	
H19	
H20	

Xylene

XYLENE

Formula C_8H_{10} $C_6H_4(CH_3)_2$ CAS no. 5476(o-xylene)

Synonyms dimethylbenzene, xylol

Appearance	colourless, highly refractive, inflammable liquid
Melting point	-49°C
Boiling point	138 - 144°C
Vapour pressure	7 torr at 20°C
Density	0.86 - 0.88 g/cm^3
Vapour density ratio (air = 1)	3.66
Solubility in water	very slightly soluble
Flash point	20 - 30°C
Ignition temperature	465 - 525°C
Inflammable mixture	1 - 7.6 vol.°/o

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	1.6 - 4 g/kg
Fish	10 - 90 mg/l
Lower water organisms	0.1 - 1 g/l

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	870	435	60	20				

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF
			A_1	A_2	A_3	Group
		4.35				S

Remarks Data refer to the commercial isomer mixture
CAS.-No 108383 (m-xylene)
CAS.-No 106423 (p-xylene)

1 mg/m^3 $\hat{=}$ 0.23ppm
1 ppm $\hat{=}$ 4.35 mg/m^3

XYLENE

Description of Material

Regular xylene is a mixture of three isomers, o-xylene (20-25%), m-xylene (50-60%) and p-xylene (20-25%). Because of the rather close boiling points, separation of the isomers presents difficulties. Therefore, they are normally not separated for industrial use. If a certain isomer is used for a synthesis, the higher boiling o-xylene is first isolated by fractional distillation, then p-xylene is frozen from its mixture with m-xylene.

Hazards to Man

The intake of xylene evokes a burning sensation in the mouth and stomach, nausea, vomiting and salivation. Even the inhalation of vapours of low concentration leads to headache, dizziness, nausea, irritation of the respiratory and gastrointestinal tracts. Higher vapour concentrations lead to intoxication and excitedness, in severe cases to unconsciousness accompanied by respiratory paralysis and cramps (Lit.1).

[illegible]ene is a flammable liquid. By evaporation poisonous and explosive mixtures are formed, which can be ignited at hot surfaces, by sparks or open flames.

Hazards to the Environment

A content of 0.3-1.0 mg/1 xylene affects the taste and smell of water. The lethal concentrations for fish vary between 10 and 90 mg/1, depending on temperature and isomers. m-Xylene shows the strongest poisonous effect (Lit.2).

XYLENE

Production and Use / Waste Formation

Xylene is obtained mainly from naturally occurring hydrocarbon sources, such as coal tar and petroleum. During coal tar distillation, xylene is found in the so-called light oil, which boils between 80 and 170°C. The various petroleum improvement methods for the production of high-grade motor fuels lead almost all to a hydrocarbon mixture with a high percentage of aromatics, of which in addition to xylene, toluene and benzene are the most desirable components. Further separation is accomplished by fractional distillation.

Xylene is mainly used as a solvent and cleaning agent and is a starting material for dyes and many organic chemicals. Fuels, especially aircraft fuels, are improved by the addition of xylene. It is also used as a carrier for spraying of pesticides.

Various quantities of xylene-containing wastes are obtained from the production and processing methods of xylene. The bulk originates in the petrochemical industry.

Waste Treatment

Diluted aqueous solutions are drained into the sewerage system in accordance with local conditions and are then subjected to a biological treatment in the sewage treatment plant. Solvents and sludges of higher concentration from which xylene cannot be recovered have to be disposed of in special waste incinerators.

Literature

1) Gleason, M.N., et al., Clinical Toxicology of Commercial Products, 3rd ed., Baltimore, Maryland: Williams and Wilkins Company 1969.

2) McKee, J.E. und Wolf, H.E. eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

Benzene

BENZENE

Formula C_6H_6

CAS no. 71432

Synonyms benzol

Appearance	colourless, highly refractive liquid with characteristic odour
Melting point	6°C
Boiling point	80°C
Vapour pressure	76 torr at 20°C
Density	0.87 g/cm^3
Vapour density ratio (air = 1)	2.7
Solubility in water	very slightly soluble (1.8g/l at 20°C)
Flash point	11°C
Ignition temperature	555°C
Inflammable mixture	1 - 8 vol.°/o

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	1 - 5.7 g/kg
Fish	5 - 37 mg/l
Lower water organisms	

Occupational safety - Danger symbols F + T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		80	10	3				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		3.5				S

Remarks Danger of resorption through the skin
carcinogenic

1 mg/m^3 ≙ 0.31 ppm
1 ppm ≙ 3.2 mg/m^3

BENZENE

Description of Material

Benzene, the base material of many aromatic compounds, is a colourless, mobile, refractive liquid of characteristic odour. It burns with a strongly sooting flame. Technical grade benzene contains as an impurity small amounts of thiophene (C_4H_4S), which can be removed by hydrogenation under pressure at 380°C with a molybdenum sulphite catalyst (desulphurization). Benzene is only slightly miscible with water, but miscible in any ratio with most organic solvents, such as ether, alcohol, acetone or glacial acetic acid.

Hazards to Man

Physiologically, benzene is a strong poison. It is readily lipoid-soluble. Upon intake in large amounts and due to accumulation in the brain, it causes excitedness, the so-called benzene intoxication, and finally narcosis. Frequent accompanying phenomena are dizziness, a sense of weakness, headaches, vomiting, cramps and respiratory paralysis. Inhalation of highly concentrated benzene vapours may cause death within a few minutes (Lit.1). Long-term exposure to smaller amounts leads to severe damage of the blood-producing system, especially bone marrow and capillaries. Moreover, it results in degeneration phenomena of various organs, such as the liver, kidneys, spleen and reproductive organs (Lit.2). Besides by inhalation, benzene may be absorbed through the intact skin. It dissolves the natural fatty layer of the skin and causes irritations, which in severe cases may progress to blistering (Lit.3).

Most of the inhaled benzene is exhaled chemically unchanged. The balance remaining in the organism is degraded by metabolism. After recovery from the sickness, an oversensitivity towards benzene frequently remains in the affected persons (Lit. 4).

Benzene can also cause alterations of the chromosomes (fragmentation). So far, however, these have only been found in body cells, not in reproductive cells (Lit.4). Results from experiments with animals have confirmed the suspicion that benzene is carcinogenic. Investigations on whether it also has mutagenic properties are still continuing.

When working with benzene, an increased fire hazard exists. Benzene in uncovered containers evaporates quickly. Together with air, easily combustible, explosive mixtures are formed. They are heavier than air and spread over the floor or the working area. Ignition can take place at hot surfaces, by sparks or open flames.

Flowing benzene causes electrostatic charges, so that fire can originate by discharge. All pipes, vessels and containers through which benzene flows or in which benzene is stored have to be earthed. Also, during pouring of benzene, funnels or similar equipment should be earthed for the same reason. Rooms in which benzene is stored should be cool and well ventilated.

Hazards to the Environment

Benzene belongs to the water-endangering substances according to VLwF, which cause great damage even in small quantities. Experimental studies on the effect of benzene on organisms have been carried out mainly with fish and mammals. Lethal concentrations determined in these investigations are for rainbow trout between 10 and 20 mg/l (Lit.5), for minnows 8-9 mg/l (in hard water at 16°C) (Lit. 6). Benzene-containing water causes a change in the taste of edible fish. Water plants are damaged by a concentration of 10 mg/l (Lit.7). The carcinogenic effect of benzene was proven successfully on mice (Lit.8).

BENZENE

Production and Use / Waste Formation

Formerly, benzene was obtained mainly by distillation of coal tar or by scrubbing from crude gas. Today it is produced from acetylene (Reppe synthesis) or by separation of hydrocarbon mixtures obtained in petroleum processing (refining).

Benzene is used as an extraction, defatting, cleaning agent and as a solvent, further for dip, brush and spray painting, for lacquer and paint removal and for staining. It is also required in the manufacture of plastics and cleansers, as a solvent for printing inks and rubber, for vulcanization, for adhesives and as an additive for heating and motor fuels. It serves, moreover, as a starting material for the preparation of important organic compounds, such as aniline dyes, alkyl benzenes, nitrobenzene, chlorobenzene, styrene, nylon, phenol, insecticides etc.

Wastes containing benzene are mainly distillation residues from petrochemistry, spent catalysts, residues from coking processes and spent solvents from petrochemistry, the reprocessing of which is frequently too expensive.

Waste Treatment

Benzene is biodegradable (Lit.9). Diluted aqueous solutions, therefore, are drained into sewage treatment plants and decomposed there by anaerobic bateria.

Solvent mixtures and sludges of higher concentration are burnt in special waste incinerators if a recovery process is uneconomical (Lit.10).

BENZENE

Literature

1) Valentin, Klosterkötter, Lehnert, Petry, Rutenfranz, Wittgens Arbeitsmedizin, Thieme Verlag Stuttgart 1971

2) Fodor, G. Schädliche Dämpfe VDI Verlag Düsseldorf 1972

3) Braun, W., Dönhardt, A. Verfigtungsregister Thieme Verlag 1970

4) Gesundheitsschädliche Arbeitsstoffe Toxikologische arbeitsmedizinische Begründung von MAK-Werten, Verlag Chemie Weinheim 1972 edited by Henschler, Würzburg

5) Steinmann, P. und Surbeck, G.: Die Wirkung organischer Verunreinigungen auf die Fauna schweizerischer fließender Gewässer. Preisschreiben der Schweiz. Zoolog. Ges. Bern 1918

6) Leclerc, E., Devlaminck, F., Bull. Trimestriel du Centre Belge d'Etude et de Documentation des Eaux Liege 15 66 - 67 1952

7) North W.J., Clendenning KA Scotten, H.L.: The effects of wastes discharges upon Kalp Quartely Prog. Report Inst. of Marine Resources Uni, of California, La Jolla, IMR Reference 60 - 10 (1 October - 31 December 1959)

8) 'Water Quality Criteria Data Book", Vol. 1, Organic Chemical Pollution of Freshwater EPA Report No. 18010 DPV 12/70, A.D. Little, Inc. December 1973

9) Hovious, J.C. Fisher, J.A. und Conway, R.A. "Anaerobic Treatment of Synthetic Organic Wastes," Water Pollution Control Research Series 12020 DIS 01/72, U.S. EPA, issued by the Union Carbide Corp.: January 1972

10) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste, issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973

Toluene

TOLUENE

Formula C_7H_8 $C_6H_5CH_3$ **CAS no.** 108883

Synonyms methylbenzene, toluol, phenylmethane

Appearance	colourless, refractive, inflammable liquid with benzenelike odour
Melting point	-95°C
Boiling point	111°C
Vapour pressure	22 torr at 20°C
Density	0.87 g/cm^3
Vapour density ratio (air = 1)	3.18
Solubility in water	slightly soluble (0,47 g/l at 16° C)
Flash point	6°C
Ignition temperature	535°C
Inflammable mixture	1.2 - 7 vol.°/o

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	1.2 - 7 g/kg
Fish	10 - 65 mg/l
Lower water organisms	60 mg/l

Occupational safety - Danger symbols F+ Xn

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
	750	750	56.4	18.8				II

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VL^{WF} Group
		18.75				

Remarks

1 mg/m^3 ≙ 0.267 ppm

1 ppm ≙ 3.75 mg/m^3

TOLUENE

Description of Material

Toluene is a colourless, highly refractive liquid of benzene-like odour. It is flammable and burns with a strongly sooting flame. Toluene is found in petroleum and coal tar besides other aromatic and aliphatic hydrocarbons. With a vapour pressure twice as high as water, toluene is to be considered a volatile substance.

hazards to Man

Poisonings from toluene are most frequently caused by inhalation of vapours. Skin contact leads less to serious poisonings, but rather to local irritations, particularly upon repeated contact with liquid toluene (rate of resorption through the skin in man: 14-23 mg/cm^2 per hour) (Lit.1). Due to its solubility in lipoids, the toluene absorbed by the body accumulates mainly in lipoid-containing organs, especially in the brain, adrenal gland, bone marrow and liver (Lit.2). In high concentrations toluene vapours cause severe irritation of the conjunctiva and mucous membranes of the respiratory tract.

Accompanying symptoms of an acute poisoning are more or less distinct disorders of the central and vegetative nervous systems, which manifest themselves in excitation and intoxication states, numbness, dizziness, headaches, general weakness, disturbance of coordination and balance, cramps and unconsciousness. Great nervousness, insomnia and muscular weariness remain on occasion several days after termination of exposure. The poisoning seldom takes a lethal course.

The complaints upon chronic poisoning are similar: irritation of mucous membranes, pains in the chest, loss of appetite, nausea and vomiting, dizziness, headaches, tiredness, nervousness and insomnia, nose bleeding and intolerance towards alcohol (Lit.3).

TOLUENE

Chronic exposure to toluene vapours may cause the so-called polisher-keratitis in the cornea. Small vacuoles are formed in the region of the eyelid margin, accompanied by inflamed alterations of the surrounding tissue (Lit.4). Further organic damage observed after long-term exposure to higher concentrations is necrosis and degeneration phenomena of various organs, especially the liver, kidneys and brain cells as well as changes in the white blood count.

In addition to these dangers to the health of man there exists due to the high inflammability of toluene an increased danger of accidents. Due to evaporation explosive mixtures are formed with air; ignition may occur at hot surfaces, by sparks or open flames. Plants which process larger quantities of toluene therefore have to be equipped with sparkproof electrical systems.

As is the case with benzene, here too exists the danger of electrostatic charging of pipes and containers through which toluene flows. They thus have to be earthed. This is also true of storage and transport vessels.

Storage areas should be cool and well ventilated.

Hazards to the Environment

Serial investigations have been carried out with mammals, fish and lower water organisms.

During inhalation studies, the following lethal doses (LD) were determined:

Mice	:	LD	35 mg/l after 2 hours	(Lit.5)
Rats	:	LD_{50}	30 mg/l after 4 hours	(Lit.6)
		LD	46 mg/l after 6.5 hours	(Lit.7)
		LD	56 mg/l after 20 min.	(Lit.8)
Rabbits	:	LD	249 mg/l after 62 min.	(Lit.6)

TOLUENE

Concentrations which caused acute poisonings in fish were, depending on temperature and species of fish, between 10 and 90 mg/1 (Lit.9); the lethal dose for rainbow trout was 10 mg/1 (Lit.10). For small crustaceans (Daphnia) and algae, danger thresholds of 60 mg/1 and 120 mg/1, respectively, were determined (Lit.11).

Production and Use / Waste Formation

Today, toluene is produced predominantly from petroleum by the refining processes for crude oil developed by the petrochemical industry, in particular dehydrogenation of cycloparaffins or aromatization of saturated aliphatic hydrocarbons. In addition, toluene is formed as a by-product during coking and can be isolated from the coal tar by fractionation.

Toluene is used in industry as a solvent for fats, rubber and resins, as a thinner for paints, lacquers and polishes, as a paint remover and cleaning agent in the graphic industry, as a strarting material in the chemical industry for synthesis of trinitrotoluene, benzoic acid, saccharin, dyes, benzene, phenol, toluene diisocyanates, synthetic leather and others. It is further used as aircraft fuel and for motor fuel mixtures with a high octane number.

Toluene wastes originate mainly in petrochemical plants as well as plants which use toluene as a raw material for synthesis of the above-mentioned compounds. Further sources of waste are installations which blend fuels and plants which utilize toluene as a solvent.

Waste Treatment

When discharging wastes of low toluene content into the sewerage system, the local discharge regulations have to be observed. Solvent wastes from which toluene cannot be recovered and toluene-containing sludges are burnt. Distillation residues and toluene-containing sludges are disposed of in special waste incinerators (Lit.13).

TOLUENE

Literature

1) Dutkiewics, T. and Tyras, H.
Skin absorption of toluene, styrene and xylene by man.
Brit. J. Industri. Med. 25 (1968) p. 243.

2) Fabre, R., Truhaut, R., Laham, S. and Peron, M.:
Recherches toxicologiques sur les solvants due
remplacement du benzene. II. Etude due toluene.
Arch. mal. profess. med. Paris 16 (1955) p. 197.

3) American Petroleum Institur (A.P.I.) Annual Report
Toxicological review toluene New York: American
Petroleum Inst. 1948, p. 46.

4) Schmidt, E.: Die Hornhauterkrankungen der
Möbelpolierer Arch. Gewerbepath. Gewerbehyg. 15
(1956) p. 37.

5) Lazarew, N.W.: Über die Giftigkeit verschiedener
Kohlenwasserstoffdämpfe, Arch. exp. Path. Pherm.
143 (1929) p. 223 (Muse).

6) Carpenter, CP., Smyth, Pozzani: Assay of acute
vapor toxicity and the grading and interpretation
of results of 96 chemical compounds. J. Industr.
Hyg. 31 (1949) p. 343.

7) Cameron, C.R. Patterson, De Saram, Thomas: The
toxicity of some methyl derivatives of benzene with
special reference to pseudocumene and heavy coal tar
naphtha J. Path. Bact. 46 (1938) p. 95.

8) Schumacher, H., Grandjean: Vergleichende Untersuchungen
über die narkotische Wirksamkeit und die akute
Toxizität von neun Lösungsmitteln. Arch. Gewerbepath.
Gewerbehyg. 18 (1960) p. 109.

9) Patterson, J.W. and Minea, R.A., "Wastewater Treatment
Technology", 2nd ed., issued by the Illinois Institute
of Technology for Illinois Institute for Environmental
Quality, February 1973.

10) Thumann, F.E: Z. Fischerei 38, (1940) p. 656-679

11) Bringmann, G., Kühn: Vergleichende wassertoxikologisch
Untersuchungen an Bakterien, Algen, Kleinkrebsen.
Gesundh.-Ing. 80 (1959) p. 115-119.

12) Römpps Chemie-Lexikon, Franck'sche Verlagsbuch-
handlung, Stuttgart, 7th edition (1973)

13) Ottinger, R.S. et al.: "Recommended Methods of
Reduction, Neutralization, Recovery or Disposal
of Hazardous Waste", 16 Vols., issued for the EPA,
TRW Systems Group, PB 224579, Set/AS 1 February 1973.

I BIOCIDES, PHARMACEUTICALS AND COMPOUNDS DERIVED FROM THEM, INCLUDING PESTICIDES

I 1
I 2
I 3
K 4
I 5
I 6
I 7
I 8
I 9
I10
I11
I12
I13
I14
I15
I16
I17
I18
I19
I20

TARS AND TAR-LIKE PRODUCTS

K 1	Carbolic Oil
K 2	Carbolineum
K 3	
K 4	
K 5	
K 6	
K 7	
K 8	
K 9	
K10	
K11	
K12	
K13	
K14	
K15	
K16	
K17	
K18	
K19	
K20	

Carbolic Oil

CARBOLIC OIL

Formula

CAS no.

Synonyms tar oil , naphtha

Appearance light yellow to dark red, oily liquid

Melting point	
Boiling point	170 - 230°C
Vapour pressure	
Density	0.86 - 0.89 g/cm³
Vapour density ratio (air = 1)	
Solubility in water	
Flash point	38°C
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		400						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		20				

Remarks

1 mg/m³ ≙ ca 0.5 ppm
1 ppm ≙ ca 2 mg/m³

CARBOLIC OIL

Description of Material

Carbolic oil is one of the four main fractions which are isolated from the crude product during coal tar distillation. It is also referred to as middle oil. Its boiling range lies between 170 and 250°C.

In addition to other hydrocarbons, carbolic oil contains predominantly naphthalene, phenol, the cresol isomers, xylenol as well as nitrogen-containing bases such as toluidine, quinoline and isoquinoline.

Hazards to Man

Because of its high boiling point, the danger of poisoning by inhalation of vapours is low. The poisonous effect upon oral intake corresponds to that of xylene (Lit.1) and is due to its content of toxic aromatics, such as benzene, phenol, cresol, xylenol, cumol, ethyl benzene etc.

Hazards to the Environment

The hazard presented to the environment by carbolic oil has not yet been investigated. The effect on animal and plant life may well depend on the contents of toxic aromatics.

Production and Use / Waste Formation

Carbolic oil is produced from coal tar by distillation at 170-230°C. It is a mixture of mainly aromatic hydrocarbons and is further processed to obtain the individual substances. The crude distillate, also known as heavy naphtha, is used for cumarone resins, as a solvent for asphalts, tars and rubber and for the production of naphtha soaps.

CARBOLIC OIL

Carbolic oil wastes are formed primarily during distillation of coal tar at asphalt producers as well as in plants which use carbolic oil as a solvent (Lit.2).

Waste Treatment

Aqueous solutions of low concentration are discharged into the sewerage system and, after prior gravity separation of the insoluble liquid layers, biodegraded in sewage treatment plants.

Solvent wastes with higher carbolic oil contents have to be disposed of in special waste incinerators (Lit.2).

Literature

1) Gleason, M.N., et al., Clinical Toxicology of Commercial Products, 3rd ed., Baltimore, Maryland: Williams and Wilkins Company 1969.

2) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 vols., issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973.

Carbolineum

CARBOLINEUM

Formula Mixture of aromatic hydrocarbons CAS no. XX8021394C

Synonyms

Appearance	brown-red oil, smells like tar
Melting point	
Boiling point	above 270°C
Vapour pressure	
Density	1.07 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	very slightly soluble
Flash point	74°C
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	0.5 - 5 g/kg
Warm-blooded animals	
Fish	1 - 20 mg/l
Lower water organisms	2 - 20 mg/l

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		22						

Water mg/l	TWVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
		0.001				

Remarks

1 mg/m^3 ≙ 0.22 ppm
1 ppm ≙ 4.4 mg/m^3

CARBOLINEUM

Description of Material

Carbolineum is a brown-red oily mixture with a tar-like odour consisting of not readily distillable coal tar constituents (tar oil). It contains, among others, anthracene, phenanthrene, phenols, cresol, naphthalene and chrysene. It is used with and without the addition of mineral dyes as a preservative coating material for wood and stone and for fighting fruit tree pests.

The most common wood preservatives made of carbolineum in Germany are:
Bekarol TP, Carbolin, Carbolineum 66 natur, Carbolineum Haltermann, Carbolineum Rütgers (Impraleum), Duxolineum P, Kulbanol P, Original-Carbolineum Rücotex I, Pigrol-Holzschutz naturbraun, Torbil, Vedag-Carbolineum, Verol-Carbolineum (Lit.1).

Hazards to Man

Carbolineum is a moderately strong poison. Upon direct contact it causes severe local irritation (acne, furunculosis). Oral intake leads to gastrointestinal disorders with nausea and vomiting, so that more serious disorders normally cannot develop. Vapours cause inflamed changes of the mucous membranes of the upper respiratory tract and bronchi. Inhalation of high concentrations leads to narcotic states with circulatory collapse and unconsciousness (Lit.1).

When working with wood preservatives on a carbolineum base, attention has to be paid to the fact that commercial products frequently contain other poisonous materials, such as arsenic, mercury, fluorine and chromium compounds and chlorinated aromatics.

These materials are not leachable, but require proper treatment.

Hazards to the Environment

The poisonous effect of carbolineum on water organisms depends mainly on the phenol and cresol content. It is influenced by the temperature and oxygen content of the water.

Fish die at concentrations of 1-20 mg/1. Lower concentrations are accumulated and stored in the fatty tissue and give a phenolic taste to edible fish (Lit.2). The same range of concentration is toxic to lower water organisms (Lit. 3).

Production and Use / Waste Formation

Carbolineum is obtained from coal tar by distillation at 260-290°C.

It is used as a wood preservative, e.g. for railway sleepers, telephone poles and posts. It is used on a large scale for fighting fruit tree pests. In this application the pure, undiluted tar oils may not be sprayed, because they would damage the plants. The commercial fruit tree carbolineum, therefore, has been emulsified by the addition of detergents, soda and lye. Before use in autumn it is highly diluted and applied to the defoliated trees and bushes. In this way moss and lichen growth, fungi and eggs of various pests are fought.

Wastes with higher contents of carbolineum are produced primarily during coal tar distillation, but also in plants which process carbolineum to wood preservatives and at the ultimate consumer.

CARBOLINEUM

Waste Treatment

Waste waters with lower concentrations of carbolineum can be purified in a biological sewage treatment plant.

To reduce the phenol content to less than 1 mg/1, chemical or physical treatment, such as ozone treatment or filtration with activated charcoal, have to follow. Concentrated wastes which cannot be reprocessed have to be disposed of in special waste incinerators.

Literature

1) W. Braun, Dönhardt A., Vergiftungsregister, Thieme Verlag 1970.

2) McKee, J.E. und Wolf, H.e., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

3) Gelsenkirchener Dokumentation, Hygiene-Institut des Ruhrgebietes, Gelsenkirchen, 1973.

L ORGANIC AND INORGANIC ACIDS, BASES AND ANHYDRIDES

L 1	Maleic Anhydride
L 2	Hydrogen Fluoride
L 3	Hydrogen Chloride
L 4	Potassium Hydroxide
L 5	Sodium Hydroxide
L 6	Nitric Acid
L 7	Sulphuric Acid
L 8	Fluosilicic Acid
L 9	Acetic Anhydride
L10	Oxalic Acid
L11	Phthalic Anhydride
L12	Benzenesulphonic Acid
L13	
L14	
L15	
L16	
L17	
L18	
L19	
L20	

Maleic Anhydride

MALEIC ANHYDRIDE

Formula $C_4H_2O_3$ $(COCH)_2O$ **CAS no.** 108316

Synonyms 2,5-furandione
2,5-dioxo-dihydrofuran

Appearance white solid substance or colourless melt

Melting point 52.6°C
Boiling point 202°C
Vapour pressure 5.10^{-5} torr at 20°C
Density 0.93 g/cm³
Vapour density ratio (air = 1)
Solubility in water slightly soluble (reacts slowly with water)
Flash point 103°C
Ignition temperature 475°C
Inflammable mixture 1.4 - 7.1 vol.°/o

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	400 - 800mg/kg
Fish	138 - 230 mg/l
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m³	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW1	TA Luft IW2	TA Luft KLS	TA Luft KLG
	0.8+)	1						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A1	ENV. 140 (EEC) A2	ENV. 140 (EEC) A3	VLWF Group
		0.05				

Remarks +) Danger of sensitization

1 mg/m³ ≙ 0.245 ppm
1 ppm ≙ 4.076 mg/m³

MALEIC ANHYDRIDE

Description of Material

In the crystalline state maleic anhydride forms colourless rhombic needles. As a commercial product the substance is shipped as white flakes, lumps or sticks or as a colourless melt in the temperature range between 55 and 60°C. The substance begins to evaporate at normal temperatures and reacts upon the addition of water to slowly form readily soluble maleic acid, which is soluble in water to 30 - 40 weight per cent.

The olfactory threshold is below 2 mg/m^3.

Hazards to Man

In the form of dusts or vapours maleic anhydride has a strong irritating effect on eyes and respiratory organs. Contact with the skin leads to painful irritations. Burns develop upon long-term exposure. Moisture increases this effect. Inhalation of vapours may cause in severe poisonings pulmonary edemas. Bronchitis and chronic inflammation of the mucous membranes of the nose and eyes may occur on repeated exposures of only 5 mg/m^3. Oral intake, even of small amounts, may cause death or permanent injuries.

In spite of the relatively high flash point of 103°C, the substance should not be heated above 70°C. Upon heating to high temperatures, explosive gas mixtures are formed. Fine maleic anhydride dust yields ignitable dust-air mixtures when dispersed in air. Ignition may be caused by hot surfaces, sparks or open flames.

When cleaning equipment (e.g. containers) of attached maleic anhydride, alkali of any kind has to be avoided.

MALEIC ANHYDRIDE

Hazards to the Environment

The acute poisoning effect of maleic anhydride/maleic acid on fish in contaminated waters has been proven. The determined lethal concentrations lie between 138 mg/l and 240 mg/l (Lit.1). The harmless concentration for fish is estimated to be 35 mg/l (Lit.2). The peroral toxicity for rats is relatively low. The lethal dose lies in the range of 400 - 800 mg/kg (Lit.3,4).

Production and Use/Waste Formation

Maleic anhydride is produced mainly by oxidation of benzene with atmospheric oxygen in the vapour phase and in the presence of catalysts (e.g. vanadium oxide on aluminium chips and diatomaceous earth). In recent times C_4-hydrocarbons such as butane and butene have been preferred over benzene as the starting material. Also, during naphthalene oxidation (phthalic acid process) and during the oxidation of toluene to benzaldehyde, maleic anhydride is obtained as a byproduct.

Maleic anhydride is used mainly (about 40 per cent) as an intermediate in the production of unsaturated polyester resins (maleate resins). It is further applied in the modification of alkyd resins, copolymers and lubricants and in the production of maleic and fumaric acids, agricultural chemicals (e.g. for the insecticide Malathion and the growth control agent maleic hydrazide), tetrahydrofuran and plasticizers.

Wastes with certain amounts of maleic anhydride and its hydrolyzation product maleic acid are the tar-like residues of the production process and the wash water from cleaning the equipment. Wastes of high concentration are off-spec batches from manufacture and quantities that became useless during transport or storage as the result of impurities. Spoilage is generally caused by hydrolysis of the material.

MALEIC ANHYDRIDE

Waste Treatment

Effluents with maleic acid contents from equipment cleaning should be neutralized with sodium hydroxide before being discharged into biological sewage treatment plants. The sodium maleate formed is quickly biodegraded.

Tar products which contain maleic anhydride, as well as wastes with high concentrations of this material, are best disposed of in special waste incinerators.

Literature

1) Gelsenkirchener Dokumentation
Hygiene-Institut des Ruhrgebietes, Gelsenkirchen 1973

2) McKee, J.E. and Wolf, H.E. (Editors)
Water Quality Criteria (2nd edition)
California State Water Resources Control Board
Publication 3 - A 1963

3) Oettel, H.
Werksärztekonferenz der Berufsgenossenschaft der Chemischen Industrie 1955
Bad Dürkheim

4) Fasset, D.W.
in Patty, F.A.: Industrial Hygiene and Toxicology
2nd rev. ed., p. 1820
Interscience Publishers, John Wiley & Sons
New York/London 1962

Hydrogen Fluoride

HYDROGEN FLUORIDE

Formula	HF
CAS no.	7664393
Synonyms	anhydrous hydrofluoric acid, hydrofluoric acid gas
Appearance	colourless gas aqueous solution: colourless, mobile liquid
Melting point	$-83.4^{\circ}C$
Boiling point	$19.5^{\circ}C$
Vapour pressure	
Density	$0.9\ g/cm^3$
Vapour density ratio (air = 1)	
Solubility in water	unlimited
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	(1mg/l chron.)
Warm-blooded animals	
Fish	40 mg/l
Lower water organisms	

Occupational safety - Danger symbols T (hydrogen fluoride)
C (hydrofluoric acid)

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1 +)	IW_2 +)	KL_S	KL_G
	2	2	0.2	0.1	0.003 (0.002)	0.006 (0.004)		

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	1.5++)		1.5++)			

Remarks +) Values for transitional regulation until 28.8.1978
++) Values for fluoride
Very poisonous, nonflammable

HYDROGEN FLUORIDE

Description of Material

At normal temperatures hydrogen fluoride is a colourless, mobile liquid, which fumes strongly in air and boils at 19.5°C. Its odour is extremely pungent. Hydrogen fluoride is miscible with water in all proportions. Dissolution proceeds with generation of considerable heat and the formation of hydrofluoric acid. The acid dissolves numerous metals, with generation of hydrogen. Gold and platinum are not attacked; lead is attacked only superficially, since the fluoride formed is very slightly soluble and protects the bulk from further attack by the hydrofluoric acid.

A remarkable property of hydrofluoric acid is its ability to attack glass. Hydrofluoric acid as well as gaseous hydrogen fluoride are used to etch glass, whereby the etched glass object remains clear with the use of acid, while it appears frosted with hydrogen fluoride. Because of this reaction with glass, hydrogen fluoride cannot be stored or transported in glass containers, but only in containers of lead, steel or plastics.

Hazards to Man

Inhalation of the extraordinarily poisonous vapours of hydrogen fluoride can lead to severe irritation and burns of the mucous membranes of the pharynx and respiratory tract prior to the formation of ulcers in the upper respiratory tract. Even a short-term exposure to concentrations of 50-250 ppm is dangerous.

Hydrofluoric acid severely burns the skin and causes very slowly healing sores. Exposure of the skin to low concentrations proceeds without warning. Reddening of the skin, pains and similar symptoms appear only after the acid has penetrated deeply into the skin, e.g. upon contact with a 20% hydrofluoric acid,pains occur only after several hours. Only then are blisters formed.

Burns on toe and finger nails, especially if the acid gets under the nails, are very painful and lead almost always to loss of the nail. Contact on these parts is particularly dangerous, because it can easily result in infiltration and subsequent destruction of the bones. Cases are known where amputation became necessary (Lit.1).

Particularly dangerous are splashes into the eye, which in most cases lead to the loss of vision.

Hazards to the Environment

Data given in the literature on the danger thresholds of hydrogen fluoride for fish vary. They extend from 40 to 60 mg/1 (Lit.2,3).

A three to four week exposure of pines, oaks and Norway maple to 0.00033% of hydrogen fluoride resulted in a discoloration of the leaves. Waterweed was damaged with a solution that contained 8 mg/1 hydrogen fluoride (Lit.4).

Since fluoride ions are formed by dissociation when hydrogen fluoride is dissolved in water, the data given for fluorides have to be observed too.

Production and Use / Waste Formation

For the production of hydrogen fluoride / hydrofluoric acid, wet or dry processed fluorspar (calcium fluoride) in finely ground form is reacted either with concentrated sulphuric acid or with bisulphate and the addition of steam and inert solid material in externally heated rotary kilns. Hydrogen fluoride is released from the reaction mixture and is compressed in watercooled lead drums.

HYDROGEN FLUORIDE

In addition, hydrogen fluoride is also formed as a by-product during superphosphate production from fluorapatite and sulphuric acid. During dissolution of the raw phosphate, part of the fluorine contained in the minerals escapes as hydrogen fluoride.

Hydrogen fluoride is used in the production of fluorides (e.g. sodium fluoride and cryolite) and organic fluorine compounds. It is a widely used catalyst in the petroleum industry and has applications in etching glass, metal pickling, enamelling and textile cleaning. Furthermore, hydrogen fluoride is used as an antiseptic, in the manufacture of electrode carbon and in the extraction of uranium.

Larger or smaller quantities of hydrofluoric acid are found in effluents of glass plants, petroleum refineries, producers of cryolite, fluorides, fluoborates and fluosilicon products, of the nuclear energy industry and producers of stainless steel. For instance, in the cryolite production of a medium-sized company a daily quantity of more than 100 m^3 of wash water is produced. This wash water is strongly acidic and contains in addition to other dissolved components especially free hydrochloric and free hydrofluoric acid.

Waste Treatment

The bulk of soluble fluorine compounds is removed from hydrofluoric acid-containing waste waters by precipitation with barium salts. A treatment with calcium hydroxide and careful stirring, and subsequent purification in sufficiently large settling tanks removes the fluorides down to a residual concentration of not more than 10 mg/l.

HYDROGEN FLUORIDE

Instead of calcium hydroxide, dry lime, e.g. waste lime from other operations, may be used; This produces a sludge containing less water.

The magnesium, aluminium and ion exchange methods have proved useful for the disposal of smaller amounts of fluorides. Magnesium hydroxide sludge is best applied in the magnesium method. In the ion exchange method it is possible to regenerate the exchange resin with a 2-5% sodium hydroxide solution; the remaining hydroxide is then neutralized with carbonated water (Lit.5).

The exhaust air from processing raw phosphate with sulphuric acid is treated in closed condensation systems with a water spray or saturated sodium chloride.

The problem of the disposal of hydrogen fluoride-containing wastes is essentially a problem of the disposal of the corresponding fluorides (see fluorides).

Literature

1) Meidl, J.H., Explosive and Toxic Hazardous Materials, London 1970, p. 256.

2) Strell, M., Allg. Fischerei - Ztg. 57 (1931), pp. 197 - 201.

3) McKee, J.E. and Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3 - A 1963.

4) Bursche, E.-M., Inaug. - Diss., Berlin 1949.

5) Sierp, Fr., Gewerbliche und industrielle Abwässer, Berlin, Heidelberg, New York 1967, p. 633.

Hydrogen Chloride

HYDROGEN CHLORIDE

Formula HCl **CAS no.** 7647010

Synonyms	anhydrous hydrochloric acid aqueous solution: hydrochloric acid muriatic acid
Appearance	colourless gas or colourless liquid
Melting point	$-114.2^{\circ}C$
Boiling point	$-85^{\circ}C$
Vapour pressure	31920 torr at $20^{\circ}C$
Density	1.639 kg/Nm^3
Vapour density ratio (air = 1)	1.30
Solubility in water	highly soluble (719.8g/l at$20^{\circ}C$)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols T (hydrogen chloride)
C (hydrochloric acid)

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1 +)	IW_2 +)	KL_S	KL_G
	7	7			0.10 (0.10)	0.20 (0.30)		

Water mg/l	TWVO	PLWS	ENV. 140 (EEC)			VLWF
			A_1	A_2	A_3	Group
						L++)

Remarks +) Preliminary value in paranthesis (Until accurate measuring technique has been established)
++) For hydrochloric acid

1 ppm $\hat{=}$ 1.515 mg/m^3
1 mg/m^3 $\hat{=}$ 0.66 ppm
nonflammable gas

174<

HYDROGEN CHLORIDE

Description of Material

Hydrogen chloride is a colourless, pungent smelling gas, which is easily compressed to a colourless liquid and sold in steel bottles.

The aqueous solution of hydrogen chloride is called hydrochloric acid. Its solubility is high. One litre of water dissolves 507 1 of hydrogen chloride at 0°C. The commercial "concentrated hydrochloric acid" is colourless, has a pungent odour and fumes in air; therefore, it is called "fuming hydrochloric acid". This hydrochloric acid has a specific gravity of 1.19 and contains 38 weight % hydrogen chloride. More diluted hydrochloric acids have lower specific gravities[+].

Hydrochloric acid can be concentrated by distillation only up to a concentration of 20% hydrogen chloride, after which a mixture of constant composition (azeotrope) distills at 110°C.

Hazards to Man

Hydrogen chloride gas attacks severely the mucous membranes of the eyes, pharynx and respiratory tract; teeth are also affected (Lit.1). These phenomena are due to the formation of hydrochloric acid.

Hydrochloric acid burns the skin and may cause immediate blindness if sprayed into the eyes. Fumes of the concentrated acid cause the same injuries as hydrogen chloride gas. In concentrations of 35 ppm they irritate the pharynx after a short time and are unbearable at 50 to 100 ppm.

[+] Notice: There is a fortuitous relationship between the percentage and specific gravity of hydrochloric acid. If the first two digits after the decimal point of the specific gravity are doubled, the corresponding percentage is obtained; an acid with specific gravity 1.16 contains, therefore, 32% HCl, one with a specific gravity 1.06 contains 12% HCl.

HYDROGEN CHLORIDE

Hazards to the Environment

The effect of various mineral acids on plants depends not only on the pH value but also on the type of anion: water which contains hydrogen chloride / hydrochloric acid in a dilution of 1 : 175 000 or about 6 mg/l inhibits growth of the radicle (Lit.2).

The lowest dose of hydrogen chloride which causes death in trout within 24 hours is reported to be 10 mg/l. However, for some species of fish the dose is as low as 3.6 mg/l. One measure of the toxicity of hydrogen chloride in water is its pH value; when lowered to 5 or below by the addition of hydrogen chloride / hydrochloric acid, its effect on fish is lethal (Lit.3). In the presence of larger quantities of iron, less acidic water (pH about 5.5) in combination with iron deposits on the gills is sufficient to cause death (Lit.4).

Hydrochloric acid is perceived by the sense of taste at concentrations of 32 mg/l (Lit.3).

Production and Use / Waste Formation

Hydrogen chloride is obtained by the following processes:

- The classical, today only rarely used method for the production of hydrogen chloride/hydrochloric acid is the conversion of rock salt with sulphuric acid in a continuous operation. The process proceeds in two steps which can also be used individually as the "Berlin HCl Process" or Mannheim HCl Process" for the production of hydrogen chloride.
- The preparation from the elements chlorine and hydrogen by reaction in quartz burners has to proceed under well controlled burning conditions due to the danger of explosion.

HYDROGEN CHLORIDE

- In the organic-chemical industry hydrogen chloride is produced as a byproduct in large quantities during the chlorination of benzene or the dehydrochlorination of dichloroethane to vinyl chloride, for example. The resulting hydrogen chloride is frequently highly concentrated, but more or less contaminated by organic additions and/or by chlorine gas.

- A further possibility for production is the reaction of chlorine and water vapour over coke at 350°C, whereby carbon dioxide is produced in addition to hydrogen chloride.

Hydrochloric acid is obtained by the following processes:

- By isothermal absorption of hydrogen chloride. This produces an impure acid; the heat of solution has to be removed by cooling.
- By adiabatic absorption; here the heat of solution is removed by the evaporation of water. This has the advantage that during vapourization organic impurities are removed and a very pure hydrochloric acid is obtained.

Hydrogen chloride is a starting material for the plastics industry (PVC production) and is used in the manufacture of chlorosulphonic acids and acetyl chlorides. Hydrochloric acid is used in the dye industry, in metallurgy, in ore processing, in petrochemistry and the petrochemical industry. Considerable quantities are also required for the production of starch and protein for the food industry.

Main sources of hydrochloric acid-containing wastes are the cooling water which is used in the absorption of hydrogen chloride gas in water and the weakly acidic effluents of waste gas scrubbers. The waste water produced can amount to 12-13 m^3 per ton of hydrochloric acid produced; its acid content is 2-10 mg/l (Lit.4). Small amounts of sulphuric acid may also be present.

HYDROGEN CHLORIDE

During the absorption of hydrogen chloride which originates from chlorination reactions in the organic-chemical industry, waste waters are produced which may contain impurities from this particular industry.

In addition to the producing industry, the HCl-processing industry contributes to waste formation. Involved are mainly users who are concerned with the production of organic and inorganic chlorides, with pickling of steel and with alkylation and polymerization of petrochemical products.

Large quantities of hydrogen chloride are produced during the incineration of chlorinated hydrocarbons at sea, a method which is at least questionable from an ecological point of view.

Waste Treatment

Neutralization of hydrochloric acid-containing effluents presents no serious difficulties; neutralization is normally carried out with a solution of soda and calcium hydroxide. After diluting with water, the sodium and calcium chlorides formed may be admitted to drainage.

Concentrated waste acids which frequently contain additional toxic substances (metal compounds) are properly disposed of in special waste disposal facilities.

Literature

1) Moeschlin, B., Klinik und Therapie der Vergiftungen, Stgt. 1972.

2) Tiegs, E. Abwasserschäden, in: SORAUER's Handbuch der Pflanzenkrankheiten, Berlin 1934

3) Bandt, H. -J Beitr. z. Wasser-, Abwasser- und Fischereichem. a.d. Flua Magdeburg I (1946), 15 - 23

4) Mckee, J.E. and Wolf, H.E. eds., "Water Quality Criteria," 2nd ed., California State Water Resources Control Board, Publication 3 - A 1963

POTASSIUM HYDROXIDE

Potassium Hydroxide

Formula KOH

CAS no. 1310583

Synonyms potassium hydrate, caustic potash
aqueous solution: potash lye

Appearance white hygroscopic lumps, pellets, flakes or white powder
aqueous solution: colourless liquid

Melting point 360°C

Boiling point 1320°C

Vapour pressure

Density 2.04 g/cm^3

Vapour density ratio (air = 1)

Solubility in water Very highly soluble (1070 g/l at 20°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols C

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A$_1$	A$_2$	A$_3$	
						L$^{+)}$

Remarks +) For potash lye
Nonflammable, very corrosive

POTASSIUM HYDROXIDE

Description of Material

Potassium hydroxide is a substance similar to sodium hydroxide and is sold as white lumps, rods or pellets.

It is strongly hygroscopic; that means it absorbs moisture from the air and deliquesces. The application of potassium hydroxide as a drying agent is based on this fact. It is also used as protection against infiltrating carbon dioxide, since this is also absorbed by potassium hydroxide.

The aqueous solution of the readily soluble potassium hydroxide is more basic than that of sodium hydroxide and is called potash lye.

Hazards to Man

The hazards presented to man by potassium hydroxide/ potash lye are very similar to those of sodium hydroxide. The heat generated when potassium hydroxide is dissolved in water may lead to the ignition of highly inflammable products stored in the vicinity. If potassium hydroxide solution comes in contact with metals such as aluminium, zinc or galvanized iron, hydrogen is released which presents the danger of oxy-hydrogen gas formation.

Potassium hydroxide/potash lye has a strongly corrosive and decomposing effect on human tissue, especially when dusts are inhaled. Oral intake causes a constriction of the esophagus (swallowing difficulties), severe pains in the throat and stomach region, vomiting of blood and collapse and leads to most severe burns, which may result in the destruction of the entire digestive tract.

POTASSIUM HYDROXIDE

Hazards to the Environment

The lowest lethal dose of potassium hydroxide for mammals upon oral intake is reported to be 43 mg/kg body weight (Lit.1). At a concentration of 28.6 mg potassium hydroxide/l minnows die within 24 hours, trout within the same period at a concentration of 50 mg/l (Lit.2). The crucial criterion for the damaging effect is the pH value, which with 9.2 indicates the beginning of the lethal region for brook and rainbow trout, perch and ruffle, while it is 10.8 for pike, carp and tench.

The injurious effect manifests itself in burns of the outer skin, swelling of gills and formation of slime.

The toxicity threshold for small crustaceans (Daphnia) lies between pH 9.1 and 9.5. Among the small water organisms rotifers cease reproduction at pH values above 9.0 (Lit. 3).

With algae an increase of pH may lead, together with other factors, to blooming-of-the-lakes or may initiate it.

Contents of 1 to 50 mg potassium hydroxide/l affect the taste of water (Lit. 2).

Production and Use / Waste Formation

Analogous to sodium hydroxide, potassium hydroxide may be obtained by electrolysis of an aqueous solution of potassium chloride by the diaphragm process as well as by the amalgam process, only the polarization voltage is somewhat higher. Application of the amalgam process requires a much more thorough purification of the salt solution, because hydrogen formation at the mercury cathode is catalyzed far more easily by impurities in the potassium amalgam. Concentration of the bath-lyes obtained is carried out by evaporation, as in the sodium hydroxide process.

Potassium hydroxide may also be obtained by the reaction of potassium carbonate with calcium hydroxide.

Because potassium chloride is about ten times as expensive as sodium chloride, potassium hydroxide is considerably more expensive and is used only in special cases.

Areas of application are, among others, the manufacture of other potassium compounds (potassium bichromate, potassium permanganate), the manufacture of liquid soaps ("green soaps"), electroplating, photogravure and lithography. Potassium hydroxide is also used as a paint and lacquer remover, wood stain and for mercerizing cotton.

During the production of potassium hydroxide by electrolysis, no actual waste waters are formed; however, upon evaporation of the electrolyte bath in multiple-effect vacuum evaporators, cooling and condensate waters are produced which are weakly to clearly alkaline (pH between 7.5 and 9).

In the manufacture of soap, waste waters, the so-called "spent lyes", may be obtained which show a clear to strong alkaline reaction. Similarly, in the above-mentioned applications waste waters may be produced which contain potassium hydroxide in various amounts.

Waste Treatment

The potassium hydroxide-containing waste waters which are obtained in production and processing may be utilized to neutralize acidic waste waters, e.g. pickling wastes, if internal conditions permit. If this is not possible, the alkaline effluent has to be neutralized with acids or acidic flue gases and may then be discharged into the sewerage system or drainage ditch. If neutralizing installations are not available in the plant and if the products cannot be utilized otherwise, the lye concentrates have to be turned over to special waste disposal facilities.

POTASSIUM HYDROXIDE

Literature

1) Davis, E.F. u.a., Water Quality Criteria Data Book, Vol.2 1971

2) Mckee, J.E. and Wold, H.E. eds., "Water Quality Criteria," 2nd ed., California State Water Resources Control Board, Publication 3 - A 1963

3) Loub, W. Umweltverschmutzung and Umweltschutz in naturwissenschaftlicher Sicht, Vienna 1975, p. 121

SODIUM HYDROXIDE

Sodium Hydroxide

Formula NaOH

CAS no. 1310732

Synonyms caustic soda, sodium hydrate
aqueous solution: soda lye

Appearance white hygroscopic lumps, granules, flakes, pellets or sticks
aqueous solution: colourless liquid

Melting point 319.1°C

Boiling point 1390°C

Vapour pressure

Density 2.13 g/cm^3

Vapour density ratio (air = 1)

Solubility in water highly soluble (420g/l at 20°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:
Man
Warm-blooded animals
Fish
Lower water organisms

Occupational safety - Danger symbols C

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
	2	2						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A$_1$	A$_2$	A$_3$	
						L

Remarks

Nonflammable, very corrosive

SODIUM HYDROXIDE

Description of Material

Sodium hydroxide forms a white, opaque, ray-like crystalline mass, which is strongly hygroscopic and also absorbs carbon dioxide from the air. It is sold in rods, chips or pellets.

Sodium hydroxide is readily soluble in water, generating a great deal of heat. The aqueous solution is strongly alkaline, is slick and soapy to the hand and is called soda lye.

If sodium hydroxide is stored for a longer period in glass containers, aluminium and silicon are dissolved from the glass. In order to avoid this, the use of polyethylene containers is recommended.

Hazards to Man

Dissolving sodium hydroxide in water generates large amounts of heat, which may be sufficient to ignite inflammable materials stored in the vicinity. Upon contact with metals such as zinc, galvanized iron and aluminium, hydrogen is released, which forms explosive mixtures with the oxygen of the air (oxy-hydrogen gas!).

Solid or dissolved sodium hydroxide is corrosive and decomposing to all body tissue. It causes burns and ulcers, which after healing leave deep scars. Therefore, solid sodium hydroxide should never be touched with bare hands.

The literature reports a case where swallowing of 30 g sodium hydroxide resulted in vomiting, exhaustion, collapse and death (Lit.1).

Fumes, vapours or dusts which contain sodium hydroxide can cause skin burns and, upon contact with the eyes, severe damage to the cornea. Inhalation leads to irritations and, further, to severe burns of the respiratory or digestive tract.

SODIUM HYDROXIDE

Hazards to the Environment

The damaging effects of sodium hydroxide in water are mostly a consequence of the increase in the pH value. Fish show no specific poisoning effect, but develop burns on the outer skin of the gills and exhibit strong slime formation. Fish perish by suffocation due to slow destruction of their respiratory organ. The lethal threshold in the alkaline range extends from 9.2 pH for brook trout to 10.8 pH for carp and tench. The sequence of sensitivity to lyes is opposite to the sequence of sensitivity to acids. Crayfish can exist for a while at pH 10.2 (Lit.2).

At concentrations of 20 to 100 mg/1 sodium hydroxide in water, salmon, trout, carp and crayfish are killed (Lit.3).

Contents of 1-50 mg sodium hydroxide /1 affect the taste of water (Lit.3).

Production and Use / Waste Formation

For the technical production of sodium hydroxide in the lime-soda process, a 10-12% solution of sodium carbonate (obtained from the Solvay process or from natural soda) is reacted, while agitated with calcium hydroxide at boiling temperature (caustification of soda). After removal of the precipitated salts a 28% lye is obtained or, after final evaporation and complete dehydration, solid sodium hydroxide is recovered.

In the diaphragm process the electrolysis of alkali-metal chlorides yields sodium hydroxide which contains small, residual amounts of sodium chloride impurities. The sodium hydroxide obtained by the amalgam process is free of sodium chloride and is purified of iron and mercury impurities by filtration through pressed nickel powder.

SODIUM HYDROXIDE

In addition, the Löwig process, in which soda and pyrite roasting slags in finely ground form are reacted in an air furnace, is also employed. Subsequently, the reaction product is decomposed by hot water to yield sodium hydroxide.

The lye obtained is transported in iron barrels or vessels, the solid material (rods, chips and pellets) in iron drums.

Sodium hydroxide is a strong base and is used industrially for numerous purposes; in soap manufacture, in chemicals and detergent production, in the dye industry, in the cellulose and paper industries, for mercerizing cotton, in the textile industry, in film production and for the manufacture of aluminium, for electroplating and petroleum refining.

During manufacture of sodium hydroxide, waste waters are produced (about 10 m^3/t sodium hydroxide) which contain primarily calcium carbonate impurities (about 170 g /l) and have a pH value of 9-10 (Lit.4).

Sodium hydroxide-containing effluents and wastes are also produced in processing industries, metal pickling plants and galvanizing shops. The wastes are frequently contaminated with heavy metals.

Waste Treatment

After neutralizing sodium-containing effluents with acids, these wastes may be discharged into the sewerage system providing it has been ascertained that no other poisonous substances are present.

Sometimes, flue gases are used for the neutralization. The gases flow in a countercurrent to the waste water through a tower filled with suitable material (e.g. Raschig rings).

SODIUM HYDROXIDE

In case neutralization - if necessary with heavy metal precipitation - cannot be carried out, there exists the possibility of turning the wastes over to a special waste treatment plant.

Literature

1) Meidl, J.H., Explosive and Toxic Hazardous Materials, London 1970, p. 272.

2) Loub, W., Umweltverschmutzung and Umweltschutz in naturwissenschaftlicher Sicht, Vienna 1975.

3) McKee, J.E. and Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3 - A 1963.

4) Koziorowski, B. and Kucharski, J., Industrial Waste Disposal, Oxford, New York 1972.

Nitric Acid

NITRIC ACID

Formula HNO_3

CAS no. 7697372

Synonyms aqua fortis

Appearance waterclear or yellowish to reddish coloured liquid, fumes in air

Melting point	-41.6°C
Boiling point	83°C
Vapour pressure	
Density	1.503 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	unlimited
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols O,C

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	25	5						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
			$50^{+)}$	$50^{+)}$	$50^{+)}$	L

Remarks +) Values for nitrate
Highly corrosive liquid, nonflammable acid

NITRIC ACID

Description of Material

Pure nitric acid is waterclear and fumes in air. When boiled - or upon irradiation with light at room temperature - nitrogen dioxide is formed which colours the solution yellow, at higher concentrations red; therefore, the name "red fuming nitric acid" refers to the solution that releases red-brown fumes.

Nitric acid is soluble in water in all proportions. Upon heating, a constant boiling (azeotrope) mixture is obtained at 121.8°C containing 69 per cent nitric acid.

Nitric acid is a strong oxidizing agent and dissolves copper, silver and mercury, for example, with the development of nitrogen oxide, while gold and platinum are not attacked. The acid is, therefore, used for the separation of gold and silver.

A number of metals, such as iron, aluminium and chromium, which actually should be dissolved by nitric acid, are not attacked. This phenomenon is called "passivation" and is explained by the formation of a thin, continuous oxide film which protects from further attack by the acid. Thus, it is possible to store and transport nitric acid in vessels and drums of stainless steel and aluminium in addition to glass bottles and ceramic containers.

Hazards to Man

As a strong oxidizing agent, nitric acid can react so vehemently that ignition takes place with many oxidizable materials such as metal powders, carbides, hydrogen sulphide, turpentine, acetic anhydride and alcohols; in violent reactions with insufficient removal of heat, explosions occur.

These facts have to be considered for storage.

NITRIC ACID

The fumes escaping from the concentrated acid consist, besides of nitric acid vapour, of a mixture of various nitrogen oxides which are poisonous and, therefore, very dangerous. When inhaled, they are often not immediately noticed, because they are not always brownish coloured. Upon accidental inhalation they can lead to pulmonary edemas, which not seldom are fatal (these oxides are formed, for example, upon contact of the acid with copper, brass, zinc, wood, sawdust, fabrics, paper and waste). The severity of the poisoning is noticed only after hours, when the lung tissue is largely destroyed. The poisoning symptoms are headache, exhaustion and lowered blood pressure. After discoloration of the mouth region and difficulty in breathing, death occurs by suffocation.

Smaller amounts of nitric acid cause itching and a yellow coloration of the skin; larger quantities of concentrated acid cause burns and poorly healing wounds which may be fatal if they extend over a larger area. Particularly sensitive are mucous membranes and the eyes, damage of which may lead to the loss of vision.

Swallowing of nitric acid causes internal irritations, burns and, in severe cases, death.

Workers who are regularly exposed to acids suffer occasionally from "acid necrosis of the teeth", that is, an anomalous deterioration of the teeth due to decalcification of the tooth substance (Lit.1).

Hazards to the Environment

The possible hazard presented to the environment by nitric acid depends - as with other mineral acids - not only on the pH but also on the nature of the anion, in this case the nitrate ion.

Sickness followed by death was observed in carp at a pH of 4.8 (Lit.2). Trout, which are even more sensitive to acids, showed damage at nitric acid concentrations of 1.6 to 20 mg/1 (Lit.3). Pike and tench are considerably less sensitive (Lit.2).

As a highly dissociated acid, nitric acid inhibits growth of radicles. The effective concentration is about 1:100 000 or about 10 mg/1 (Lit. 4).

Possible poisonous effects on fish as the result of nitration have been investigated primarily using sodium nitrates; the corresponding data can be found in Lit. 5, 6 and 7.

Production and Use/Waste Formation

Production of nitric acid from Chile saltpetre and calcium nitrate by reaction with sulphuric acid is, as the oxidation of nitrogen, of no technical significance. The method applied today consists of the oxidation of ammonia to nitric oxide, its further oxidation to nitrogen dioxide and subsequent reaction with water.

Two methods are applied for the oxidation of ammonia: first, oxidation with air on a platinum/rhodium catalyst at about 900°C, and, secondly, oxidation with pure oxygen on a platinum/rhodium catalyst under pressure (5 - 7 atm) and temperatures of 800 - 850°C.

Due to the azeotropic mixture with water a 69 per cent acid at best can be obtained by rectification; a distillation with concentrated sulphuric acid is thus used for further concentration. Instead of sulphuric acid, a concentrated solution of magnesium nitrate may also be used.

Nitric acid is used in the fertilizer industry, for the production of ammonium nitrate, calcium nitrate and sodium nitrate, for the processing of raw phosphates, for the manufacture of heavy-metal nitrates, for the

NITRIC ACID

separation of silver and gold, for the etching of metals, in the explosives industry and as a component for rocket fuels.

A 98 - 99 per cent nitric acid in combination with sulphuric acid gives nitrating acid, a much used nitrating agent in organic chemistry, in particular for organic intermediates and for gunpowder and explosives.

The manufacture of concentrated nitric acid produces waste water of 80 - 90 m^3/t acid. The main impurities are nitric acid and sulphuric acid, which together are present in a quantity of about 3 g/l (Lit.8).

Cooling waters are practically free of impurities and, therefore, are recirculated. They may become contaminated by acids in case of a technical malfunction or an accident in the plant. In addition to the producer, various amounts of nitric acid-containing waste waters and waste concentrates are produced by the processing industry.

Waste Treatment

The waste waters produced during production or processing of nitric acid may be discharged either directly where the drainage conditions permit or after prior neutralization. Neutralization may be accomplished with soda, sodium hydroxide or calcium hydroxide. If internal neutralization installations are not available, nitric acid wastes have to be turned over to special waste treatment plants.

NITRIC ACID

Literature

1) Moeschlin, S. Klinik and Therapie der Vergiftungen, Stuttgart 1972

2) Schäperclaus, W. Zeitschr. f. Fischerei 24 (1926), p. 493

3) McKee, J.E. and Wold, H.E. eds., "Water Quality Criteria," 2nd ed., California State Water Resources Control Board, Publication 3 - A 1963

4) Tiegs, E. Abwasserschäden, in: SORAUER's Handbuch der Pflanzenkrankheiten, Berlin 1934

5) Greif, Fr. Abwasserbeseitigung and Gewässerverunreinigung in: Handbuch der Binnenfischerei Mitteleuropas, Vol. IV, 3rd edition, Stuttgart 1928

6) Jones, R.E. Journ. Exp. Biol. 16 (1939), pp. 425 - 437

7) Denzer, H.W. Merkblatt über die Schädigung der Fischerei durch Abwasser, Landesanstalt f. Fischerei Nordrhein-Westfalen 1961

8) Koziorowski, B. and Kucharski, J. Industrial Waste Disposal, Oxford, New York 1972, p. 144

Sulphuric Acid

SULPHURIC ACID

Formula H_2SO_4

CAS no. 7664939

Synonyms oil of vitriol

Appearance colourless, oily liquid

Melting point 10.4°C (100°/o acid)

Boiling point 338°C (98.3 °/o acid)

Vapour pressure

Density 1.84 g/cm³

Vapour density ratio (air = 1) 3.4

Solubility in water unlimited

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols C

Safety guidelines

Air mg/m³	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW₁	TA Luft IW₂	TA Luft KL$_S$	TA Luft KL$_G$
	1		0.2	0.1				

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group
	240+)		250+)	250+)	250+)	l

Remarks +) Values for sulphate

Highly corrosive liquid, nonflammable

SULPHURIC ACID

Description of Material

Pure sulphuric acid is an oily, immobile, colourless and odourless liquid. Upon heating, fumes rich in sulphur trioxide escape initially, until finally at a constant boiling temperature of 338°C a 98.3% sulphuric acid (azeotropic mixture) distills. Therefore, a 100% sulphuric acid cannot be obtained by distillation of dilute sulphuric acid, but only by dissolution of the required quantity of sulphur trioxide in concentrated sulphuric acid. The acid obtained in this manner is also referred to as monohydrate; it is able to dissolve additional amounts of sulphur trioxide, forming fuming sulphuric acid (oleum).

Sulphuric acid is hygroscopic, has a very great affinity for water and is miscible with water in all proportions, generating considerable heat.

Concentrated sulphuric acid chars many organic materials (paper, linen, fabrics).

Upon reaction with less noble metals such as zinc, aluminium and magnesium, hydrogen is generated, which can reduce concentrated acid partly to hydrogen sulphide. The more noble metals, e.g. copper, mercury and silver, dissolve in sulphuric acid upon heating, with the release of sulphur dioxide. Platinum and gold are not attacked.

Since sulphuric acid is very corrosive and attacks practically all metals to a certain degree, only certain containers are acceptable for storage and transport. Glass is used for all concentrations; rubber- and leadlined containers are used for dilute acid (lead forms with sulphuric acid insoluble lead sulphate which protects from further attack). Iron or steel tanks are utilized for high acid concentrations.

SULPHURIC ACID

Hazards to Man

Due to the generation of large amounts of heat, mixing of sulphuric acid with water can lead to vehement splashing of acid. In this way large areas of the skin, including the eyes, may be burned or charred; shock and collapse also occur. Working with concentrated sulphuric acid always requires the wearing of safety goggles, rubber gloves and solid shoes. Dilution of sulphuric acid with water has to proceed always so that the acid is added to the water in a thin jet with constant agitation. Never the other way around!

Addition of concentrated sulphuric acid to chlorates, carbides, nitrates, picrates, permanganates as well as oxides and hydroxides of alkali and alkaline earth metals and concentrated ammonia can lead to violent reactions which may progress explosively.

Since contact of less concentrated sulphuric acid with iron causes the release of hydrogen, the atmosphere above sulphuric acid which is stored or transported in iron or steel containers may contain explosive mixtures (oxy-hydrogen gas!). It is further possible that these mixtures contain the highly poisonous hydrogen sulphide.

At temperatures above 50°C sulphur trioxide fumes, which form heavy, white smoke with air, escape from sulphuric acid. The fumes provoke cough and at concentrations of 0.1% make breathing almost impossible. Inhalation of concentrated vapours or fumes causes unconsciousness and severe injuries to the lungs. Workers who are regularly exposed to acids suffer occasionally from "acid necrosis of the teeth", that is, an anomalous deterioration of the teeth due to decalcification of the tooth substance (Lit.1).

SULPHURIC ACID

The hazards to persons working with fuming sulphuric acid (oleum) are many times greater than to those working with straight sulphuric acid.

Hazards to the Environment

The sulphuric acid concentrations which are poisonous or lethal to fish lie, for an exposure time of 24 hours, between 6 mg/l for trout and 24.5 mg/l for Leponis Machrochirus, a perch species from the North American lakes (Lit.2). The poisonous effect is due mainly to the acid, expressed in the pH value. Obvious effects on fully grown fish can be observed at pH values below 5 (Lit. 2,3).

Sulphuric acid inhibits the growth of radicles in a dilution of 1:65 000 or 15 mg/l (Lit.4). Low acid concentrations cause a decrease in the water up-take in plants; transpiration is stimulated by low acidity and inhibited by higher acidity.

Possible poisonous effects caused by the sulphate ion have been investigated mainly with sodium and ammonium sulphate. Data on these investigations with fish are reported in Lit.5,6 and 7.

Production and Use / Waste Formation

Two processes are common for the preparation of sulphuric acid: The Lead Chamber Process, which has been used since the middle of the 18th century, but is only rarely applied today and yields primarily an acid of 80%, and the Contact Process, which yields acid of any desired concentration up to oleum. Both methods start with sulphur dioxide, which is obtained by oxidation of elemental sulphur or hydrogen sulphide, by roasting of sulphidic ores (e.g. pyrite, sphalerite, chalcopyrite and galena), by reduction with coke of waste sulphuric acid from petroleum refineries and, on a smaller scale, by reaction of sulphates, in particular gypsum, with coke and sand

SULPHURIC ACID

The sulphur dioxide obtained by these various methods is oxidized by air to sulphur trioxide, the anhydride of sulphuric acid. In the lead chamber process, nitrogen oxides, in the contact process vanadium compounds, serve as catalysts and oxygen transfer compounds. In the contact process, the sulphur trioxide produced is first absorbed by the concentrated sulphuric acid, which is subsequently diluted with water to give sulphuric acid, while in the lead chamber process, sulphur trioxide is directly reacted with water in the lead chambers.

Sulphuric acid is used in the cellulose and rayon industries, for metal processing and in petroleum refineries, for the production of inorganic acids (such as phosphoric acid, hydrofluoric acid, hydrochloric acid and boric acid), as battery acid (lead battery), in the production of various sulphates (ammonium, sodium, aluminium, zinc and copper sulphate), of titanium dioxide, silica gel, detergents (alkyl sulphonates), caprolactam, citric acid, synthetic rubber, naphthol and explosives. Sulphuric acid is required for the production of superphosphate, for the drying of gases and for uranium ore processing.

During the manufacture of sulphuric acid, waste problems occur at various points of the production process. Plants which obtain their sulphur dioxide by oxidation of sulphur produce waste gases which contain sulphur dioxide and sulphur trioxide and which, after scrubbing, are found in the waste water.

If the sulphur dioxide is obtained from roasting of sulphidic ores, slags remain which, if dumped and not further processed for valuable metals, give off free sulphuric acid and sulphates to rainwater seepage due to the action of air and water.

SULPHURIC ACID

If the sulphur dioxide for the contact process originates from roasting of sulphidic ores, the roast gases have to be subjected to scrubbing for the removal of the smallest particles and contact poisons. As a result, a contaminated wash-acid is produced with a high content of precipitable materials and an acid content of normally below 20%.

In the lead chamber process, cooling waters are produced with a not inconsiderable acid content (up to 1 g/l SO_3) (Lit.8).

Similar acid-containing cooling waters are obtained during reprocessing of waste sulphuric acid, as in petroleum refineries during purification of lubricating oils, also during the fabrication of benzene, of explosives, in metal pickling plants, during purification of resins and saccharification of cellulose.

Waste Treatment

A portion of the waste acid is reduced to sulphur dioxide either according to the American CHEMICO process or by the process of the Farbenfabriken BAYER AG (this in particular for the waste acid from titanium dioxide production). The sulphur dioxide is returned to sulphuric acid production.

Sulphuric acid-containing effluents have to be neutralized, if necessary before their discharge into the drainage ditch. For this, simple neutralization and filtration techniques may be applied.

Larger quantities of sulphuric acid wastes which cannot be returned to a production process are best turned over to special waste disposal facilities. The thin acid from TiO_2 production (about 9% H_2SO_4 + 14% $FeSO_4$) is discharged under control into the North Sea with permission of the Deutsches Hydrographisches Institut (German Hydrographic Institute).

SULPHURIC ACID

Literature

1) Moeschlin, S., Klinik and Therapie der Vergiftungen, Stuttgart 1972.

2) Patterson, J.W. and Minea, R.A., "Wastewater Treatment Technology", 2nd ed., issued by the Illinois Institute of Technology for the Illinois Institute for Environmental Quality, February 1973.

3) Schäperclaus, W., Zeitschr. f. Fischerei 24 (1926), p. 493

4) Tiegs, E., Abwässerschäden, in: Sorauers Handbuch der Pflanzenkrankheiten, Berlin 1934.

5) Weigelt, C., Vorschriften für die Entnahme and Untersuchung von Abwässern and Fischwässern, Berlin 1900.

6) Scheuring, L. and Stetter, H., Jahrbuch vom Wasser 18 (1950/51, pp. 78 - 100.

7) D. Krauss, Zeitschr. f. Fischerei 34 (1936), pp 787 - 817.

8) Meinck, F., Stooff, H. and Kohlschütter, H., Industrieabwässer, Stuttgart 1968, p. 235.

Fluosilicic acid

FLUOSILICIC ACID

Formula H_2SiF_6

CAS no. 1309451

Synonyms Silicofluoric acid, hydro-silicofluoric acid, hydro-fluosilicic acid

Appearance Colourless gas or, in aqueous solution, colourless liquid that does not attack glass

Melting point

Boiling point 108.5°C

Vapour pressure

Density

Vapour density ratio (air = 1)

Solubility in water freely soluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	

Remarks Strong acid, equivalent to sulphuric acid

Description of Material

Pure, anhydrous fluosilicic acid is so unstable that it decomposes into silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF) immediately after formation. In an aqueous environment, SiF_4 is immediately reconverted into fluosilicic acid. In this manner, a relatively constant concentration of fluosilicic acid is maintained in aqueous solution. The commercially available concentrations are 13.3 and 30 - 35%. If this aqueous fluosilicic acid is heated, decomposition takes place immediately, releasing hydrogen fluoride. Fluosilicic acid is a strong acid that forms some slightly soluble salts with hydroxides and carbonates.

Hazards to Man

As most fluorine compounds, fluosilicic acid (H_2SiF_6) and its salts are highly toxic. Their toxicity is based mainly on the release of free hydrofluoric acid after uptake into the body. Ingestion of the acid or it salts is accompanied initially by all signs of acid poisoning, corrosive burns of the mucous membranes, bodily pain, vomiting, diarrhea and formation of ulcers. These are quickly accompanied by the typical symptoms of fluorine poisoning. These are based on removal, to a high degree, of calcium from the body by the fluoride ion, this causing severe disturbances of cell metabolism (tetany symptoms, auricular fibrillation, blocking of the sugar metabolism and other damage).

The body looses large amounts of water and sodium chloride in a short period of time as the result of vomiting and diarrhea, and there is the hazard of a life-endangering collapse. If no treatment takes place, the fatal oral dose is 1 - 2 g for H_2SiF_6.

Chronic poisonings have been observed above all in workers who handle fluorine compounds daily (cryolite workers).

In the early stages of chronic poisoning, typical band or spot-like enamel defects on the teeth appear; later, bone changes, especially of the pelvis, spinal column and ribs, occur. However, they develop after 2 - 3 years at the earliest. As a consequence of the increasing formation of bone and the associated restriction of bone marrow, anemia might develop. In addition, there is a general loss of strength, which may result in the inability to work, in poisoned individuals (Lit. 1).

Hazards to the Environment

The toxic action of fluosilicic acid corresponds to that of hydrofluoric acid and its derivatives. Sodium fluorosilicate dust is fatal to guinea pigs after 6 hours' inhalation of a concentration of 33 mg/m^3 (Lit. 2).

In the vicinity of fluorine plants, typical harm to plants and wildlife has been observed; this can be ascribed in particular to the silicon tetrafluoride emitted (Lit. 3).

There have also been numerous observations of harm to grazing cattle in the vicinity of aluminium plants as the result of fluorine-containing waste gases, and to cattle pastures that have become contaminated through the use of smoke catridges during military exercises (Lit. 1).

Production and Use/Waste Formation

If a pure product of high percentage (30 - 35%) is desired, fluosilicic acid is produced from silicon dioxide (quartz powder) and 70 - 95% hydrofluoric acid, after adding some H_2SiF_6 as an initiator. Another possibility is the reaction of barium silicon tetrafluoride with sulphuricacid. In this case, the fluosilicic acid released must be passed into water immediately to prevent

Fluosilicic acid of low percentage is a byproduct in the production of phosporic acid and superphosphates (artificial phosphate fertilizer) from fluorine- and silicon-containing apatites. This process is accompanied by the formation of SiF_4-containing waste gases. These are removed by scrubbing with water or dilute sulphuric acid in spray towers, the SiF_4 being converted to fluosilicic acid.

Free fluosilicic acid is used in the production of aluminium fluoride from aluminium oxide or clay as well as in the production of artificial silicon oxide-free cryolite. Superphosphates are granulated and cement and mortar hardened by addition of fluosilicic acid.

The salts of fluosilicic acid (fluorosilicates) are important as wood preservatives, and to a certain degree as pesticides and disinfectants as well, because of their toxic action.

In a few countries, drinking water low in fluorine is fluorinated with fluosilicic acid to protect against carries (not in the Federal Republic of Germany). Fluosilicic acid wastes occur above all in artificial phosphate fertilizer factories as well as in the production of fluorine compounds such as metallic fluorosilicates, cryolite and aluminium fluoride (Lit. 4).

Waste Treatment

Solutions from scrubbing the waste gas as well as other solutions that contain fluosilicic acid are neutralized with a strong alkali (caustic soda) and converted into slightly soluble salts (e.g. Na_2SiF_6). If small amounts are involved, the filtered, compact salt sludges can be used together with household refuse for sanitary landfill. Larger amounts of waste are best disposed of in dumps for special waste. The neutral liquid left over is generally diverted into the sewerage system (Lit. 5).

Literature

1) Moeschlin, Klinik und Therapie der Vergiftungen, Thieme Verlag 1972

2) Weber, H.H., Engelhardt, W.E. Zbl. Gewerbehyg. Unfallverhütung 10, 41, 1933

3) Ullmann, Encyclopädie der technischen Chemie Bd. 15, p. 747

4) Encyclopedia of Chemical Technology 2nd ed. John Wiley & Sons, Inc. 1963

5) Patterson, J.W. und Minea, R.A. "Wastewater Treatment Technology", 2nd ed. issued by the Illinois Institute of Technology for Illinois Institute for Environmental Quality, February 1973. (available from NTIS, PB 216162)

Acetic anhydride

ACETIC ANHYDRIDE

Formula $C_4H_6O_3$ $(CH_3CO)_2O$ **CAS no.** 108247

Synonyms Ethanoic anhydride

Appearance Colourless, pungent liquid

Melting point	-73°C
Boiling point	140°C
Vapour pressure	4 torr at 20°C
Density	1.08 g/cm^3
Vapour density ratio (air = 1)	3.52
Solubility in water	freely soluble (100 g/l at 20°C)
Flash point	49°C
Ignition temperature	330°C
Inflammable mixture	2.0 - 10.2 vol.%

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	20	20						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLwF Group
		1.0				

Remarks

1 mg/m^3 ≙ 0.25 ppm
1 ppm ≙ 4 mg/m^3

Description of Material

Acetic anhydride is a colourless, pungent liquid that causes tears. It dissolves slowly in cold water, while dissolution at the boiling point is accompanied by a violent reaction and the formation of acetic acid.

Hazards to Man

The harmful action of acetic anhydride corresponds to that of acetic acid. Ingestion of concentrated solutions causes a typical acid poisoning with bodily pain, bloody vomiting, cardiac disorders, difficulty in breathing (acute asthmatic bronchitis), renal and circulatory insufficiency, and collapse. Similar disorders occur after inhalation of concentrated vapours. Corrosive burns may appear on the skin and mucous membranes, the eyes and upper respiratory tract being most susceptible. Repeated contact with the skin causes inflammatory changes. Chronic poisoning is characterized by gastric and intestinal disorders, loss of weight and anemia (Lit. 1). When processing acetic anhydride, it should be remembered that reactions with water, alcohols, amines and similar substances can take place very vigorously if not cooled.

Hazards to the Environment

In an aqueous environment, acetic anhydride is converted to acetic acid. Brief exposure to max. 5000 mg/l is used to treat infected fish (Lit. 2). The fatal concentration for brook trout in the case of long-term exposure (more than 24 hours) is 50 mg/l. Daphnia show the first symptoms of poisoning at 150 mg/l (Lit. 3).

Production and Use/Waste Formation

Two methods having good yields have come into use for the production of acetic anhydride:

- In the Wacker process, acetic anhydride is produced by reacting ketene with glacial acetic acid (yield 95%).

- In the Knapsack process, the bulk of acetic anhydride is produced by oxidation of acetaldehyde with atmospheric oxygen in ethyl acetate on a copper and cobalt acetate catalyst at 50 - 70 °C/4 atmg (yield 66%).

Acetic anhydride is used in organic synthesis as an acetylating agent, e.g. in the production of pharmaceuticals (acetylsalicylic acid, acetanilide, sulphonamides, vitamin B_6, acetylcholine chloride, nitrofuran), dyes and, above all, acetyl cellulose.

Large amounts of acetic anhydride or acetic acid can be expected in the waste flow from plants manufacturing cellulose acetate fibres and plastics. In waste water of the pharmaceutical industry, acetic anhydride is unimportant compared to the other waste.

Waste Treatment

Large amounts of acetic anhydride are best incinerated. By reaction with water, however, dilute solutions of acetic acid, which can be biodegraded in sewage treatment plants, can also be formed (Lit. 4).

Literature

1) Braun, W. und Dönhardt, A. Vegiftungsregister, Thieme Verlag, Stuttgart 1970

2) McKee, J.E. und Wolf, H.E. eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963

3) Anderson, B.G. Sewage Works J. 18, 82-87 (1946)
16, 1156 (1944)

4) Patterson, J.W. und Minea, R.A. "Wastewater Treatment Technology, 2nd ed., issued by Illinois Institute of Technology for Illinois Institute for Environmental Quality, Feb. 1973

Oxalic acid

OXALIC ACID

Formula $C_2H_2O_4$ HOOC-COOH **CAS no.** 144627

Synonyms none (in English)

Appearance Colourless crystals that break up to form a white powder

Melting point	189.5 °C (sublimes above 100 °C)
Boiling point	
Vapour pressure	
Density	1.9 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	very highly soluble (90 g/l at 20 °C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	1 g/kg
Fish	0.02-1 g/l
Lower water organisms	0.02- 1 g/l

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
		1						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A$_1$	A$_2$	A$_3$	
		0.05				

Remarks Danger of resorption through the skin

Description of Material

Oxalic acid is a colourless and odourless substance that crystallizes well. It breaks up in air to form a white powder. The usual, commercially available form is the dihydrate ($H_2C_2O_4 \cdot 2H_2O$), which can be converted into the anhydrous acid by dry heating to a temperature of 100°C. This substance is highly hygroscopic and sublimes above 100°C. Oxalic acid is a strong acid. It has reducing properties and decomposes to carbon dioxide and water relatively easily.

Oxalic acid accumulates in the form of alkali and alkaline earth salts in many plants, giving them their typical,acidic taste (common and sheep sorrel, wood sorrel (shamrock), types of salicornia, beet leaves, spinach, rhubarb, among others. Oxalic acid also forms in animal and human bodies as a decomposition product during sugar metabolism.

Hazards to Man

Oxalic acid has a strong, local irritating action on the mucous membranes. Ingestion of higher concentrations, both of the acid and of the soluble salts, causes corrosive burns in the mouth, esophagus and stomach with accompanying symptoms such as nausea, bloody vomiting, severe bodily pain, muscular twitching, overexcitedness and cramps. They are caused by extraction of large amounts of calcium from the blood by the oxalate ion. Acute cardiac and circulatory disorders (collapse) may be delayed symptoms, while renal obstruction and uremia may develop later as the result of accumulation of calcium oxalate in the kidneys. As little as 5 g of oxalic acid or calcium oxalate can be fatal to man.

Industrial diseases resulting from oxalic acid are caused above all by its local, inflammatory action.

Continued inhalation of concentrated vapours causes inflammation of the upper respiratory tract (bronchitis). Pains are noticed in the hands after only a few days of repeated contact with oxalic acid solutions (working without protective gloves). These pains are caused by severe damage to vessels in the fingertips. There is the danger that such damaged limbs must be amputated (Lit. 1).

Hazards to the Environment

In animal experiments, the local, vessel-damaging gangrenous action could already be detected after 7 days of one-hour exposure daily to an about 2.5% oxalic acid solution (Lit. 2).

The toxic effect on fish is noticeable at concentrations that shift the pH value of the environment into the acid region (below 5); 100 mg/l are fatal to trout.

For more sensitive types of fish, the toxicity threshold is approx. 20 mg/l.

Production and Use/Waste Formation

The most important process used to produce oxalic acid is thermal dehydrogenation of sodium formate to sodium oxalate. In addition, catalytic oxidation of ethylene glycol with oxygen is of importance. Large amounts of oxalic acid occur as a byproduct in the production of citric acid by fermentation of sugar (biotechnical utilization of the citric acid cycle - cleavage of oxaloacetic acid by the corresponding hydrolase).

A considerable amount of the oxalic acid production is used as a textile auxiliary (finishing, decolouring, cleansing of textiles). Further, it is of importance in the bleaching of stearin, bleaching and tanning of leather, rust removal (e.g. dissolution of rust in car radiators), as an auxiliary printing medium in indigo printing and in photography as a component of developers.

Oxalic acid is used further in the manufacture of various dyes (aurin, malachite green), blue inks (solution of Prussian blue) and metal cleaning agents.

It can also be used as a catalyst, precipitating agent for the rare earths, for galvanizing, in the production of various technically important oxalates, for the synthesis of certain esters as well as in the Kolbe synthesis of dicarboxylic acids from olefins.

Oxalic acid wastes occur primarily in the production of pure oxalic acid, in particular as the result of recrystallization. But large amounts of useless oxalic acid solutions also occur in the textile and metal industries. Other sources of oxalic acid wastes are plants that use oxalic acid to synthesize special carbonyl or caboxyl compounds (Lit. 3).

Waste Treatment

Small-scale users usually divert their slightly concentrated waste water into the sewerage system directly. Low concentrations of oxalic acid are biodegraded to a sufficient degree by means of the activated sludge method.

It should, however, be noted that oxalic acid inhibits the activity of microorganisms. As little as 46 mg/l cause a 50% inhibition (Lit. 4).

Larger amounts are neutralized with limestone, insoluble calcium oxalate forming. This decomposes into carbon dioxide and calcium dioxide upon burning (Lit. 3).

Larger batches of concentrated oxalic acid must be handled in treatment plants for special waste.

Literature

1) Fairhall, L.T., Industrial Toxicology, The Williams & Wilkins Camp, Baltimore 1957.

2) Holstein, E., Schädigungen durch Oxalsäure und Kleesalz bei Einwirkung auf die Haut, 13th Int. Conference on Industrial Medicine NY 1960.

3) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 Vols., issued for EPA, TRW Systems Group, PB 224579, Set/AS, 1 February 1973.

4) McKee, J.E. und Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

Phthalic anhydride

PHTHALIC ANHYDRIDE

Formula $C_8H_4O_3$ $C_6H_4(CO)_2O$ **CAS no.** 95449

Synonyms 1,3-dioxo-phthalan, phthalandione

Appearance White flakes or colourless melt (140°C)

Melting point	131°C
Boiling point	284°C (sublimes)
Vapour pressure	15 torr at 150°C
Density	1.53 g/cm^3
Vapour density ratio (air = 1)	5.1
Solubility in water	very slightly soluble
Flash point	150°C
Ignition temperature	580°C
Inflammable mixture	1.7 - 10.5 vol.%

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	0.8 - 1.6 g/kg
Fish	5 mg/l no effect
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	5	12						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.6				

Remarks

1 mg/m^3 ≙ 0.166 ppm

1 ppm ≙ 6 mg/m^3

Description of Material

Phthalic anhydride is available commercially in the form of white flakes or as a hot, colourless melt (140°C). Sublimation takes place above the melting point. The sublimate consists of white, needle-shaped crystals. A eutectic is formed together with 2% phthalic acid. The solubility in water is very low, but hydrolysis to phthalic acid does take place, slowly at normal temperatures but very rapidly at higher ones.

Hazards to Man

The toxicity of phthalic anhydride (phthalic acid) is about the same as that of salicylic and benzoic acids. Local skin and mucous membrane irritation are most prominent (Lit. 1). Liquid phthalic anhydride often causes burns with blistering and poorly healing wounds, because of its high temperature (above 130°C). But solid, crystalline phthalic anhydride causes irritation of the skin, especially moist skin.

Inhalation of dusts or vapours of this substance causes symptoms of irritation such as coughing, sneezing and increased secretion by the mucous membranes. The mucous membrane of the eyes is especially endangered. Chronic harmful effects as the result of intake of phthalic anhydride have not been observed to date. This substance is eliminated via the urine almost quantitatively as the acid. Kidney disorders do occur, however, after prolonged intake of high doses (Lit. 2).

Depending on the production process, technical phthalic anhydride contains more or less maleic anhydride and naphthoquinone. Both products are much more toxic, are highly irritating to the skin and, in addition, sensitizing. Disorders such as asthma and asthmatic bronchitis that occur should not be ascribed to the action of phthalic anhydride, but rather to that of naphthoquinone and maleic anhydride (Lit. 3).

Hazards to the Environment

Inhalation of approx. 10 mg/l of pure phthalic anhydride causes no noticeable harmful effects in cats, rabbits and guinea pigs (Lit. 4).

Unpurified phthalic anhydride with the impurities mentioned (0.04% naphthoquinone) causes an allergic reaction on the skin of guinea pigs (Lit. 5). For ingestion of phthalic anhydride, the LD_{50} is approx. 4500 mg/kg for rats and 1000 mg/kg for rabbits; repeated doses of 500 mg/kg caused inflammation of the intestine and an increase in blood urea in rabbits. Death occurred after 3 - 4 doses. Cats tolerate 200 mg/kg up to 24 times without harmful effects (Lit. 6).

Only very few results are available concerning the toxic action on aquatic animals. The LD_{50} for a certain kind of minnow is 56 mg/l (Lit. 7).

Production and Use/Waste Formation

Nowadays, phthalic anhydride is generally produced on a technical scale by oxidation of naphthalene and o-xylene in a flow of air with the aid of catalysts, in particular vanadium pentoxide.

It is used in large amounts for the synthesis of alkyd resins and unsaturated polyester resins as well as to obtain the diesters of monovalent alcohols; these are important in the plastics industry as plasticizers. Further, phthalic anhydride is the starting material for a number of dyes such as rhodamine, eosine, fluorescein, phenolphthalein, hydron yellow, quinoline yellow as well as substituted anthraquinone.

Di- and tetrachlorophthalic acid are important dye intermediates in the production of halogen-free benzoic acid, anthranilic acid and phthalimide. In tanning, sulphophthalic acid is used as a deliming agent, while its iron salt is used as a tanning agent.

Metal salts of phthalic acid are used as pigments in the paint and rubber industries. The metal complexes of pthalocyanines produced from phthalic anhydride are important pigment dyes. Terephthalic acid is obtained by isomerization of potassium phthalate.

Phthalic anhydride occurs as a waste in the solutions remaining after separation and purification of the reaction products from the production and further processing of the above-mentioned compound. Large amounts occur in plants that manufacture the following products: plastics, artificial resins, plasticizers, wetting agents and chemicals derived from phthalic anhydride.

Waste Treatment

Phthalic anydride hydrolyses slowly in water to form phthalic acid. After being neutralized with sodium salt, the acid can be fed to a normal biological waste water treatmont plant.

Larger amounts of concentrated wastes are disposed of in incinerators for special waste (Lit. 8).

Literature

1) Condensed Chemical Dictionary, 8th ed., New York: Van Nostrand Reinhold Company 1971.

2) Williams, R.T.: "Detoxication Mechanisms", 2nd ed., p. 373 Chapman and Hall, London 1959.

3) Kito, T. a. Tosu: Acute Dermatitis in a Factory Producing Phthalic Anhydride, J. Sci. Labor (Japan) 29.625 (1953).

4) Menschick, H.: Gesundheitliche Gafahren bei der Herstellung von Phthalsäureanhydrid. Arch. Gewerbepathol. Gewerbehygiene 13, 454 (1955).

5) Oettel, H.: Werksärzte-Konferenz der Berufsgenossenschaft der chem. Industrie 4./5./6. 1955 Bad Dürkheim.

6) Zeller, H.: Werksärzte-Konferenz der Berufsgenossenschaft der chem. Industrie 4./5./6. 1955 Bad Dürkheim.

7) "Water Quality Criteria Date Book", Vol. 1, Organic Chemical Pollution of Freshwater, EPA Report No. 18010 DPV 12/70, A.D. Little, Inc. December 1973.

8) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 volumes, issued for the EPA, TRW Systems Group, PB 224579, Set/AS, 1 February 1971.

Benzenesulphonic acid

BENZENESULPHONIC ACID

Formula $C_6H_6SO_3$ $C_6H_5SO_3H$ **CAS no.** 98113

Synonyms none

Appearance Colourless needles or flakes that deliquesce in air

Melting point	65 - 66°C
Boiling point	
Vapour pressure	
Density	
Vapour density ratio (air = 1)	
Solubility in water	very highly soluble
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	0.4-3.2 g/kg
Fish	400 mg/l
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		$5^{+)}$						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	

Remarks +) the value was obtained from similar compounds

(TRW)

220<

Description of Material

Benzenesulphonic acid crystallizes from aqueous solution as the monohydrate in the form of deliquescent needles. The hydrate melts at 45 - 46°C, the anhydrous acid at 65 - 66°C. It is very highly soluble in water and alcohol, slightly soluble in benzene, and insoluble in ether and carbon disulfide.

Benzenesulphonic acid is a strong acid, comparable to sulphuric acid. As it is difficult to keep it anhydrous, it is isolated in practice by "salting out" as the sulphonate by means of saturated sodium chloride solution.

Hazards to Man

Benzenesulphonic acid is a strong acid and thus causes local irritation when it comes in contact with the skin. Upon ingestion or inhalation, typical acid poisoning with corrosive burning of the mucous membranes occurs. Further effects are not known (Lit. 1).

The exhaust air from the sulphonation process used to produce benzenesulphonic acid and its derivatives can contain both unreacted aromatics (benzene, phenol, etc.) as well as sulphur trioxide. Special attention must thus be given to ventilation or exhaust equipment on the reaction vessels (Lit. 2).

Hazards to the Environment

Preliminary animal experiments indicate only moderate toxicity, but on the other hand severe irritation of the skin and mucous membranes (Lit. 3).

Production and Use/Waste Formation

Benzenesulphonic acid is produced by the sulphonation of benzene. Fuming sulphuric acid (oleum) or sulphur trioxide serves as the sulphonating agent.

Nowadays, benzenesulphonic acid is often used in place of sulphuric acid in acidic catalysis. It is used in chemical synthesis to insert sulphonate groups to make substantive dyes, pharmaceuticals and other products water-soluble. The sodium salts of alkylated, aromatic sulphonic acids with alkyl groups containing 10 - 14 carbon atoms (tetrapropylenebenzenesulphonates) are important in the detergent industry, because their potassium and magnesium salts are water-soluble and thus effective in hard water.

Bezenesulphonic acid wastes, which are always accompanied by large amounts of sulphuric acid, are found in the waste water from the production of benzenesulphonic acid and the synthesis of phenol by means of sulphonation of benzene. Smaller amounts of benzenesulphonic acid are contained in the waste water from production of resorcinol and the above-mentioned chemicals.

Waste Treatment

Benzenesulphonic acid is biodegradable. However, process waste water consisting of mixtures may react differently to bacteria than the pure substances contained in it. It must thus be checked beforehand that the process waste water can be handled by a biological sewage treatment plant, or whether the organic components must be destroyed by wet oxidation or incineration after removing the bulk of the water (Lit. 2).

Literature

1) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 vols., issued for the EPA, TRW Systems Group, PB 224579, Set/AS, 1 February 1973.

2) Ullmann, Encyclopädie der technischen Chemie, 4th edition, volume 8, page 416, Verlag Chemie, Weinheim 1964.

M	METALS, METALLIC COMPOUNDS or metal-containing inorganic or organic compounds of the following metals:
M 1	Mercury
M 2	Lead
M 3	Arsenic
M 4	Beryllium
M 5	Antimony
M 6	Chromium
M 7	Selenium
M 8	Cadmium
M 9	
M10	
M11	
M12	
M13	
M14	
M15	
M16	
M17	
M18	
M19	
M20	

Mercury

MERCURY and MERCURY Compounds

Formula Hg

CAS no. 7439976

Synonyms none

Appearance Silvery, liquid metal at normal temperatures

Melting point -38.9°C

Boiling point 357.3°C

Vapour pressure $1.2 \cdot 10^{-3}$ torr

Density 13.59 g/cm^3

Vapour density ratio (air = 1)

Solubility in water 20-30 ppm in O_2-containing water

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.1	0.05					I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	0.004	0.005	0.001	0.001	0.001	

Remarks

Mercury(II)chloride

Formula $HgCl_2$ **CAS no.** 7487947

Synonyms Corrosive sublimate, mercuric chloride

Appearance White crystals

Melting point 277 - 280°C

Boiling point 302°C

Vapour pressure

Density 5.44 g/cm^3

Vapour density ratio (air = 1)

Solubility in water highly soluble (7.4 g/l / 20°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	5 - 50 mg/kg
Warm-blooded animals	10 - 37 mg/kg
Fish	0.008 - 1.49 mg/l
Lower water organisms	0.04 - 4.7 mg/l

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	0.1	0.05					I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
	0.004	0.005	0.001	0.001	0.001	

Remarks +) here as mg/l mercury

Mercury(II)sulphate

Formula $HgSO_4 \cdot 2\ H_2O$

CAS no. 7783359

Synonyms none

Appearance White, crystalline powder

Melting point decomposes

Boiling point

Vapour pressure

Density 6.47 g/cm^3

Vapour density ratio (air = 1)

Solubility in water decomposes

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.1	0.05					I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
	0.004	0.005	0.001	0.001	0.001	

Remarks +) here as mg/l mercury

Mercury(II)nitrate

MERCURY and MERCURY Compounds

Formula $Hg(NO_3)_2$

CAS no. 10045940

Synonyms Mercuric nitrate

Appearance Large, colourless, deliquescent crystals

Melting point 70-79°C (decomposition)

Boiling point

Vapour pressure

Density 4.3 g/cm^3

Vapour density ratio (air = 1)

Solubility in water very highly soluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	0.015 mg/l
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.1	0.05					I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VL^WF Group
			A_1	A_2	A_3	
	0.004	0.005	0.001	0.001	0.001	

Remarks +) here as mg/l mercury

Description of Material/Use

Mercury is a silvery, liquid metal that already evaporates noticeably at room temperature. Because of its special properties (high density, electrical conductivity, large coefficient of thermal expansion, amalgam formation), it has many technical applications, for example in thermometers, manometers of all kinds, valves, mercury air pumps, electric switches, mercury vapour lamps and heavy-duty rectifiers, tooth fillings (silver amalgam), in the separation of metallic mixtures (lead, zinc, aluminium, bismuth), as a cathode in the electrolysis of alkali-metal salts and as a catalyst in some organic syntheses, and further in the preparation of mercury compounds.

Mercury(II)chloride (corrosive sublimate) is a translucent, radiated-crystalline substance. It is highly soluble in water, very highly soluble in alcohol (100 g of alcohol dissolve about 50 g) and quite soluble in many other inorganic solvents. Mercury(II)chloride can be purified easily by distillation ("sublimation"). It is the classical disinfectant for surgical instruments. Additional uses:
As a catalyst, to preserve wood, in the dressing of furs as well as as a negative intensifier in photography.

Mercury(II)nitrate forms large, colourless, deliquescent crystals and is very highly water-soluble. The pure aqueous solution hydrolizes slowly to form mercury(II) oxide and nitric acid. It is used for the nitration of organic aromatic compounds (e.g. mercuric fulminate $Hg(CNO)_2$).

Mercury(II)sulphate ($HgSO_4$) forms white, stellate flakes or lemon-yellow, slightly soluble powder (basic mercury sulphate $HgSO_4 \cdot 2HgO$). It serves as a catalyst in acetylene chemistry and as an electrolyte for galvanic batteries (mercury cells).

Organic Mercury Compounds

A large number of organic mercury compounds have been used because of their fungicidal action. Today there is a worldwide effort to curb their use and forbid completely at least the most toxic compounds (ethyl mercury derivatives).

Use of the following mercury compounds as seed disinfectants was still allowed in the Federal Republic of Germany in 1975:

Methyl mercury benzoate
Methyl mercury pentachlorophenolate
Ethyl mercury phosphate
Methoxyethyl mercury silicate
Phenyl mercury chloride
Phenyl mercury acetate (use no longer approved in 1975)
Phenyl mercury pyrocatechol

Dimethyl mercury, a highly volatile liquid, is produced from all mercury compounds by bacteria under certain conditions. Mercury is retained in the organism in this form.

Hazards to Man

Ingested (metallic) mercury is nontoxic, but not inhaled mercury vapour. Mercury compounds, too, are also highly toxic, the organic compounds having the greatest toxicity.

Acute poisoning can result from breathing in mercury vapours or ingesting mercury compounds. In a fatal case, the amount of evaporated mercury was 2.5 g, corresponding to 0.2 cm^3 (Lit. 1).
The fatal dose for mercury(II)chloride (corrosive sublimate) varies between 0.2 and 1 g (Lit. 2). Upon intake of 1.2 to 8.5 mg/m^3 the first indications are a metallically sweet taste in the mouth, combined with nausea and burning in the gullet. Excessive salivation, abdominal pains, diarrhea, kidney failure and damage to the central

nervous system occur after hours or days.

Organic mercury compounds induce a similar clinical picture at first. Later, damage to the nervous system is more prominent (paralysis, speech and sight disorders, impaired hearing).

The acute form can be transformed to the chronic, as mercury is retained in the body and expelled only slowly. The chronic form of the illness is brought about as the result of intake of relatively small amounts of mercury over a longer period of time (approx. 1 mg/day for vapours (Lit. 3), about one tenth of this for organic mercury compounds). Nonspecific general symptoms such as weakness and pains in the limbs are followed gradually by typical nervous disorders: over-excitedness, trembling hands (handwriting sample!), speech disorders and general emotional instability. In the advanced stage, mercury poisoning is incurable and results in death.

Precautionary measures taken at the workplace are the best protection against industrial poisoning. These include, among others, good ventilation, the wearing of dust masks, rubber gloves and shoes, personal hygiene and medical supervision. Mercury poisoning suffered as the result of a specific occupational activity is considered an occupational disease.

A general hazard to man results, above all, from the substantial build-up of mercury in moving up the biological food chain (see Hazards to the Environment). Poisoning of large numbers of people who ate mercury-contaminated fish is known from Japan. There was (is?) an acute danger to the population of other areas (Lit. 4).

In 1972 459 people died in Iraq after eating seed treated with methyl mercury. As mercury penetrates the placenta, unborn children may also be endangered. Methyl mercury is mutagenic and teratogenic (Lit. 5).

In the USA the weekly intake of mercury from food may not exceed 0.3 mg, with a maximum of 0.2 mg in the form of methyl mercury (specified in mg of mercury) (Lit. 6).

Hazards to the Environment

All forms of mercury, whether as metal, metal vapour, inorganic or organic compound, represent a burden on the environment. Regardless of the form, it is converted into methyl mercury by certain soil bacteria and/or fungi and injected into the biological food chain. The animal body is likewise capable of converting mercury vapour and mercury compounds into methyl mercury ($Hg(CH_3)_2$ or CH_3HgCl). This methyl mercury is passed on and concentrated in the biological food chain. The resulting hazard to man has already been pointed out.

The toxic properties of organic mercury compounds ($R\text{-}Hg^+X^-$) are generated by the cation $R\text{-}Hg^+$. The anion X^- determines the physical data such as solubility, vapour pressure, melting point etc. The alkyl compounds ($R=CH_3$, C_2H_5 etc.) and the alkoxy compounds (e.g. $R=CH_3\text{-}O\text{-}C_2H_4$) have the greatest and least toxicity respectively for warm-blooded animals. The aryl compounds (e.g. R=Phenyl) are of similar toxicity as the alkyl compounds, but occupy a middle position because of their low tendency to accumulate and good metabolizability.

No plants or animals that need mercury in any form for their existence are known to date. Accordingly, the amount tolerated is low. The growth of plankton is reduced to one-half by 1 ppb; all growth stops at 50 ppb (Lit. 7).

According to KLOKE and SCHENKE, 50 ppm in the soil impair the growth of plants (Lit. 8). Soils with more than 1000 ppm must be considered toxic.

In fish the critical concentrations are 0.008 mg Hg/l, 0.05 mg $HgCl_2$/l and 0.015 mg $Hg(NO_3)_2$/l (Lit. 9). These values vary with the temperature, salt content, pH value of the water, anions associated with the mercury, presence of synergistic substances such as copper or zinc, and concentration of dissolved oxygen.

Organic mercury compounds are several times more toxic than inorganic mercury compounds. The acute, fatal dose for ingestion of mercury alkyl compounds is between 12 and 20 mg/kg for mammals and birds. The decline in population of many kinds of wild birds in Sweden in the mid-1950's could be traced to the use of methyl and ethyl mercury compounds as seed disinfectants, both acute poisoning and reduction of the reproduction rate being responsible (Lit.10). No other substances having as wide-ranging a fungicidal activity as that of organic mercury compounds are known to date.

Production; Waste Formation

Mercury is found in nature primarily in the form of mercury sulfide (HgS, cinnabar). The cinnabar-containing ores are roasted in shaft furnaces while introducing air, and the escaping mercury vapours are condensed in water. The mercury recovered in this manner is already very pure (> 99%).

Mercury(II)sulphate ($HgSO_4$) is produced by heating mercury together with concentrated sulphuric acid. It is then crystallized out of the sulphuric acid solution.

Mercury(II)chloride ($HgCl_2$) is obtained on a technical scale by heating mercury sulphate and sodium chloride. The mercury(II)chloride produced sublimes and is collected.

Mercury(II)nitrate ($Hg(NO_3)_2$) crystallizes out of the solution of mercury in hot, concentrated nitric acid.

Organic mercury compounds can be prepared relatively simply:

- Mercury or a sodium amalgam is reacted with alkyl (aryl) halides;
- Benzene and phenols react with mercury acetate (direct mercuration) to yield aryl mercury acetates and mercury diaryls respectively.

There are in addition a number of special methods used to prepare individual compounds (Lit. 1o, 11, 12).

Metallic mercury is given off during the electrolysis of alkali-metal salts (in the sludge and as an impurity in sodium hydroxide, chlorine and hydrogen), zinc recovery (zinc amalgam), as a silver amalgam in dentistry (fillings), during the use of electrical equipment or measuring instruments containing mercury, and when burning coal and paper.

Inorganic mercury compounds occur in the wash water used in the electrolysis of alkali-metal salts and, further, as consumed catalysts, in the form of mercury(II)chloride and mercury(II)sulphate, in acetylene chemistry when producing vinyl chloride, vinyl acetate and acetaldehyde.

Organic mercury compounds are used in the paper industry to protect the shreaded, floating cellulose (pulp) from being attacked by bacteria, fungi and algae (slimicide). The sodium hydroxide solution used further on in the production process can also contain mercury. The waste water produced there is, it is true, very dilute, but there is a great deal of it. Additional areas of application include leather tanning and the pharmaceutical and paintindustries. The mass poisoning at Minimata, Japan was caused by methyl mercury chloride which originated as the result of an error in the production of acetaldehyde.

Waste Treatment

The mercury escaping into the gas phase during the electrolysis of alkali-metal salts is condensed by cooling to approx. 5°C. Condensation by means of water vapour and separation of the residual mercury through the use of special filters (Purasiv process, Lit. 14) represents another possibility.

In addition, mercury can be oxidized with sodium hypochlorite, and the mercury ions are subsequently removed through ion exchange.

Mercury-containing waste water can be treated using the Ventron process. The organically bound mercury is converted into inorganically bound mercury by chlorine and precipitated with sodium borohydride (Lit. 15).

The storage of mercury sulfide, the least soluble mercury compound, on special dumps should be monitored, as the microorganisms mentioned are also capable of converting mercury sulfide into soluble methyl mercury.

Burned-out fluorescent tubes, which contain up to 80 mg Hg each, can be disposed of on dumps for household rubbish as long as there are no dump-related reasons (glass breakage) opposing this. The same holds for other small devices containing mercury metal where recovery of the metal is no longer worthwhile (fever thermometers, relays etc.).

Literature

1) Lewin: Gifte und Vergiftungen, p. 258, 1928. Quoted in: Flury, F., Zernik, F.: Schädliche Gase, Springer Publishing Co., Berlin 1931 (reprinted in 1969).

2) Moeschlin, S.: Klinik und Therapie der Vergiftungen. Georg Thieme Publishing Co., Stuttgart 1972, p. 75.

3) Göthlein, Hygien. Rdsch. 21, 390 (1911).

4) Förster, U., Müller, G.: Schwermetalle in Flüssen und Seen als Ausdruck der Umweltverschmutzung, Springer Publishing Co., Berlin 1974.

5) "Water Quality Criteria Data Book", Vol. 2, Inorganic Chemical Pollution of Freshwater, EPA Report No. 18010 DPV 07/71, A.D. Little, Inc. July 1971.

6) Health Hazards of the Human Environment, edited by 100 specialists in 15 countries, Geneva: World Health Organization 1972.

7) Harriss, R.C.: Ecological implication of mercury pollution in aquatic systems, Biol. Concerv. 3, 2779-283 (1971).

8) Kloke, A., Schenke, H.D.: Quecksilber und Cadmium in Boden und Pflanze. Symposium on the problems of contamination of man and his environment by mercury and cadmium, Luxembourg, 3-5 July 1973, Luxembourg: CCE 1973.

9) "Control of Spillage of Hazardous Polluting Substances", Battelle Memorial Institute, Federal Water Quality Administration, Report 15090 FO2 10/70, November 1970.

10) Borg, K. et al: Alkylmercury poisoning in terrestrial Swedish wildlife. Viltrevy 6 (1969) 301-377.

11) Gmelin, Mercury, Part B, System no. 34, p. 1277, Verlag Chemie, Weinheim, 1968.

12) Rochow, E.G. et al: The Chemistry of Organometallic Compounds, New York - London 1957, p. 114.

13) Spengler, Frömmel et al in: Brennstoff-Chemie 37 (1956).

14) "Paring Mercury Pollution", Chemical Engineering, pp. 70, February 22, 1971.

Other literature employed (with detailed literature data):

Koronowski, P.: Nebenwirkungen von Quecksilberverbindungen auf Mensch und Tier (Sammelreferat), Mitteilungen aus der Biologischen Bundesanstalt für Land- und Forstwirtschaften Berlin-Dahlem, No. 153, Nov. 1973.

Saha, J.G.: Significance of mercury in the environment, Residue Reviews No. 42, Springer Publishing Co., Berlin 1972.

"Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste". Environmental Protection Agency, Contract No. 68-03-0089, Report No. 21485-6013-Ru-00, Vol. VI, Feb. 1973.

Mercury and the environment. Studies of mercury use, emission, biological impact and control. Organisation for Economic Co-operation and Development, Paris 1974, (OECD)

Lead

LEAD and LEAD Compounds

Formula Pb **CAS no.** 7439921

Synonyms

Appearance Bluish-grey, soft, ductile heavy metal

Melting point	327.5°C
Boiling point	1745°C
Vapour pressure	
Density	11.34 g/cm^3
Vapour density ratio (air = 1)	>1
Solubility in water	virtually insoluble
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
	0.2	0.15	0.01	0.003			I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A$_1$	A$_2$	A$_3$	
	0.04	0.05	0.05	0.05	0.05	

Remarks

1 mg/m^3 ≙ 0.116 ppm

1 ppm ≙ 8.611 mg/m^3

Lead(II)acetate

Formula $Pb(CH_3COO)_2$ $Pb(CH_3COO)_2$ **CAS no.** 301042

Synonyms Sugar of lead, acetate of lead

Appearance White powder or colourless crystals

Melting point	280°C (melt decomposes)
Boiling point	
Vapour pressure	
Density	3.25 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	highly soluble (443 g/l at 20°)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	10 - 50 mg/kg
Warm-blooded animals	120-300 mg/kg
Fish	0.4-2.8 mg/l
Lower water organisms	

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
	0.2	0.15	0.01	0.003			I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A$_1$	A$_2$	A$_3$	
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb 239<

1 mg/m^3 ≙ 0.116 ppm

1 ppm ≙ 8.611 mg/m^3

Lead(II)carbonate

Formula $PbCO_3$

CAS no. 1319466

Synonyms White lead, Kremnitz white, ceruse;
Naturally occurring mineral: cerussite, white lead ore

Appearance White powder or colourless crystals

Melting point decomposes above 315°C

Boiling point

Vapour pressure

Density 6.6 g/cm^3

Vapour density ratio (air = 1)

Solubility in water virtually insoluble (2mg/l at 20°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	10-50 g
Warm-blooded animals	120-300 mg/kg
Fish	
Lower water organisms	

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.2	0.15	0.01	0.003			I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb

Lead(II)chloride

Formula $PbCl_2$

CAS no.

Synonyms Horn lead, Pattinson's white lead;
Naturally occurring mineral: cotunnite

Appearance White, silky needles, horn-like substance or white powder

Melting point 501°C

Boiling point 950°C

Vapour pressure

Density 5.85 g/cm^3

Vapour density ratio (air = 1)

Solubility in water very slightly soluble (1 g/l at 20°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals 1.5 - 2 g/kg

Fish 0.5 mg/l

Lower water organisms

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	0.2	0.15	0.01	0.003			I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb

Lead(II)nitrate

Formula $Pb(NO_3)_2$

CAS no. 10099748

Synonyms Nitrate of lead

Appearance White powder or colourless crystals

Melting point decomposes above 470°C

Boiling point

Vapour pressure

Density 4.53 g/cm^3

Vapour density ratio (air = 1)

Solubility in water highly soluble (500 g/l at 25°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals 2 g/kg

Fish 10 - 260 mg/l

Lower water organisms 3 - 170 mg/l

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
	0.2	0.15	0.01	0.003			I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb

Lead(II)oxide

Formula PbO

CAS no. 1317368

Synonyms Lead monoxide, litharge, massicot (yellow), Lithargite (red)

Appearance Yellow or red powder, also crystalline flakes or lumps

Melting point	888°C
Boiling point	1470°C
Vapour pressure	
Density	approx. 9.4 g/cm^3
Vapour density ratio (air = 1)	>1
Solubility in water	virtually insoluble (0.1 g/l at 25°C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	0.4-2.0 g/kg
Fish	5 g/l
Lower water organisms	6.5-7.8 g/l

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
	0.2	0.15	0.01	0.003			I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb

Lead(II,IV)oxide

Formula Pb_3O_4 **CAS no.** 1314416

Synonyms Lead(II)orthoplumbate(IV), red lead, minium,
Red lead oxide, red oxide of lead

Appearance Red powder

Melting point decomposes at approx. 500°C
Boiling point
Vapour pressure
Density 9.1 g/cm^3
Vapour density ratio (air = 1)
Solubility in water virtually insoluble (9 mg/l at 25°C)
Flash point
Ignition temperature
Inflammable mixture

Toxicity range for short-term exposure:
Man
Warm-blooded animals 0.2g/kg (rats)
Fish
Lower water organisms

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.2	0.15	0.01	0.003			I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb

Lead(II)sulphate

Formula $PbSO_4$

CAS no.

Synonyms Lead vitriol
Natually occurring mineral: anglesite, lead spar

Appearance White powder or colourless crystals

Melting point	decomposes at 1170°C
Boiling point	
Vapour pressure	
Density	6.3 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	virtually insoluble (45 mg/l at 25°C; 56 mg/l at 40°C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	2 - 35 g/kg
Fish	25 mg/l
Lower water organisms	

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
	0.2	0.15	0.01	0.003			I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A$_1$	A$_2$	A$_3$	
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb

Tetraethyllead

Formula $C_8H_{20}Pb$ $Pb(C_2H_5)_4$ **CAS no.** 78002

Synonyms Lead tetraethyl, ethyl fluid, ethyl plumban, tetraethyl plumban

Appearance Colourless, oily, heavy liquid

Melting point	-136°C
Boiling point	78°C
Vapour pressure	5 - 35 torr at 20°C
Density	1.65 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	virtually insoluble
Flash point	approx. 94°C
Ignition temperature	
Inflammable mixture	1.8 vol.%

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	17 - 55 mg/kg
Fish	0.2 - 2.0 mg/l
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
	0.075	0.10						

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb

1 mg/m^3 ≙ 0.116 ppm
1 ppm ≙ 8.611 mg/m^3

Tetramethyllead

Formula $C_4H_{12}Pb$ $(CH_3)_4Pb$ **CAS no.** 75741

Synonyms Lead tetramethyl, methyl plumban, tetramethyl plumban

Appearance Colourless, oily, heavy liquid

Melting point	-30°C
Boiling point	110°C (decomposes)
Vapour pressure	22.5 torr at 20°C
Density	
Vapour density ratio (air = 1)	
Solubility in water	virtually insoluble
Flash point	37.8°C
Ignition temperature	
Inflammable mixture	1.8 vol.%

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3 +)	**MAK**	**TLV**	**MIK**		**TA Luft**			
			1/2 h	**24h**	**IW$_1$**	**IW$_2$**	**KL$_S$**	**KL$_G$**
	0.075	0.15						

Water mg/l +)	**TwVO**	**PLWS**	**ENV. 140 (EEC)**			**VLWF Group**
			A$_1$	**A$_2$**	**A$_3$**	
	0.04	0.05	0.05	0.05	0.05	

Remarks +) calculated as Pb

1 mg/m^3 ≙ 0.116 ppm
1 ppm ≙ 8.611 mg/m^3

Hazards to Man (Lit. 1-7)

The health hazard of lead has been known for a long time but has been often underestimated up to the present. Lead does not have to be dissolved to be toxic. The toxicity of lead compounds depends on their solubility in bodily fluids, the fineness of the particles and the manner in thich they enter the body, because these factors affect absorption into the blood and attack of certain organs. Lead can enter the body in three ways: through inhalation of dusts, vapours, fumes and fine mist; through ingestion with water, food and beverages; through absorption of organolead compounds directly through the skin. Contact with lead articles and inorganic compounds is harmless as long as they are not placed in the mouth or inhaled.

Lead in the form of dusts and vapours that have reached the respiratory tract is more easily resorbed than lead in the digestive tract. Because of its poor solubility and low resorbability through the gastro-intestinal lining, metallic lead, as well as most of its inorganic compounds, seldom cause acute poisoning.

The organolead compounds are much more dangerous, because those that are industrially important are fat-soluble and are resorbed into the bodily fluid very quickly, even through the skin. Their primary points of attack are the nervous system and adrenal glands. There is, however, no reason to assume basically different effects, at the place of activity, for the lead alkyls than for inorganic lead compounds.

Sicknesses caused by lead and its compounds are considered occupational diseases that must be reported. Lead that has been absorbed by the organism is, it is true, eliminated in time, primarily in the urine, but this process is so slow that lead can accumulate in the body until symptoms and invalidity appear. The slow poisoning action of small doses of "sugar of lead" (lead acetate) has been known for ages.

Acute lead poisoning causes vomiting, abdominal pains, and perhaps collapse and unconsciousness. Mees' bands, whitish lines 1 to 2 mm wide across the finger and toe nails, can appear after acute poisoning.

Chronic poisonings resulting from sustained ingestion or inhalation of small amounts are much more characteristic of the action of lead. They often occur epidemically with initially nonspecific symptoms such as general weakness, fatigue, lack of appetite, headache, continued constipation, loss of fat and weight. Characteristic symptoms of advanced poisoning are abdominal pains and sensitivity, gastric and intestinal colic ("lead colic") combined with kidney damage, circulatory disorders, raised blood pressure, anemia and simultaneous discolouration of the skin ("lead complexion"), tremors, muscular weakness, pain in the joints and muscles, gradual paralysis of the hands and arms, damage to the nervous system.

Lead acts as an enzyme poison that blocks vesicular breathing and attacks mainly the nerve cell, in addition to blood corpuscles and bone marrow, so that such nervous lesions can manifest themselves as impairments of emotional development, in particular in infants and small children (Lit. 8). Even the unborn child is endangered in this respect, as lead can pass through the placenta to the growing fetus (Lit. 9). Lead, too, is claimed to be mutagenic for man and mammals. In the elderly a mobilization of the lead stored in the bones can be expected as a result of the start of conversion processes in the bone.

Hazards to the Environment

The environmental hazard of metallic lead and inorganic lead compounds is limited, as lead is capable of forming a number of slightly soluble to virtually insoluble compounds, in particular lead carbonate (in the basic region), lead sulphate (in the acidic region) and lead sulphide(in a reducing atmosphere), so that inorganic lead discharged into the air or water has the tendency to be deposited in soils and sediments. Accordingly, animals as well as man are endangered by dusts, fumes, vapours and lead compounds dissolved in water on their way from the source of emission to the place of deposition.

Only little data is available on the effects of inorganic lead salts on plants. Lead acetate and lead nitrate are a special hazard to water because of their high solubility. Irrigation of oat and potato crops with water having a lead nitrate concentration greater than 50 mg/l resulted in the death of all plants (Lit. 11).

Lead in water is a common cause of lead poisoning of breeding animals, which are harmed much more often by lead than by other metallic toxins. It has been observed that chronic lead poisoning of animals occurs already at a lead concentration of 0.18 mg/l in soft water. The maximum value in drinking water for cattle is specified as 0.5 mg/l (Lit. 12).

The acute toxicity in the case of fish and lower water organisms is greater than that in warm-blooded animals. Lead is toxic to fish because it leads to formation of a mucous film on the gills and thus suffocation. A concentration of dissolved lead of only 0.1 mg/l has been found harmful to fish; 0.6 mg/l can already have acute toxic effects (Lit.13). The toxicity in the case of fish decreases with the hardness of the water, as dissolved lead can form slightly soluble compounds with carbonate and sulphate (Lit. 11.)

As components of lead-bearing dusts, slightly soluble lead compounds represent a hazard to the environment, because they can be inhaled or deposited on plants, thus being consumed along with the food by plant-eating animals. Lead-bearing deposits from the air and in the soil do not, of course, consist of metallic lead, but rather partly of organic, and mainly of slightly soluble inorganic compounds such as lead sulphate and carbonate (Lit. 15, 16).

According to EPA estimates, 90% of the lead in the air originates from motor fuel, from which lead is released as lead chloride and bromide during combustion.

Descriptions of Material/ Production and Use / Waste Formation

A. Lead and inorganic lead compounds

Lead in the refined state is a shiny white metal which assumes a matt, grey appearance and becomes resistant to subaerial agents and sulphur dioxide upon exposure to air as the result of formation of a protective film of basic lead carbonate or lead sulphate. Lead is virtually insoluble even in pure, air-free water. On the other hand, in the presence of oxygen in the water it oxidizes slowly and is converted into lead hydroxide. The presence of carbon dioxide increases the solubility, while hard water (bicarbonate, sulphate) and some inorganic acids such as hydrofluoric acid, sulphuric acid, phosphoric acid and dilute hydrochloric acid as well as chlorine and hydrogen sulphide reduce the corrodibility of lead by forming protective coatings. In contrast, lead is attacked by nitric acid, concentrated hydrochloric acid and most organic acids such as acetic acid, for example, as well as by alkalies such as bleaching agents, lime mortar and cement because of the amphoteric nature of lead oxide. In an acidic environment below pH 1.5 lead dissolves with the simultaneous generation of hydrogen.

The most common starting material for the extraction of lead is sulphidic lead concentrate, while oxidic lead ores are only of little importance. Nowadays, the crude lead bullion is extracted from the concentrate using the reduction roasting method. The gases from roasting are cleaned of the air-borne dust by gas cleaning systems. The usual electric dust removal systems attain an efficiency of better than 90% today. The metal-bearing dusts are usually returned to the process. The sulphur dioxide is removed by scrubbing and usually used to produce sulphuric acid. The metal-containing slags and other fused products as well as the intermediate products of pyrometallurgical crude lead refining and the anode sludges from electrolytic refining are processed in part or to a greater extent to extract the metal. The residues ought to be quite free of lead and other valuable metals, in general, but are not absolutely metal-free. Soft lead and lead hardened by adding antimony (hard lead) as well as various alloys are used in the production of storage batteries (about 40%), cable sheathing, lead sheet, foils, pipes, uniformly leaded coatings, weights, projectiles and small shot, chemical equipment such as lead chambers and acid evaporating dishes, soundproofing and radiation shields, solder, bearing metals and type metal for printing and as an addition to brass and bronze. Insofar as they are not routed to a recovery plant as lead shot, lead and semifinished products are lost in the environment as the result of wear and tear or occur as waste.

Lead acetate and related compounds are colourless salts that are highly soluble in water and also dissolve in glycerine and alcohols. The name "sugar of lead" refers to the appearance and the sweet taste. The aftertaste is metallically tart. Aqueous solutions of the basic acetates are called "vinegar of lead". Lead acetate is very poisonous.

It is produced by dissolving lead oxide in acetic acid, serves as a drying agent in paints, is used for the lead coating of metals and as a starting material for the production of other salts such as lead chromate and lead carbonate.

Lead borate, lead metaborate monohydrate $Pb(BO_2)_2 \cdot H_2O$, is a white powder or colourless crystals. It is virtually insoluble in water and alkali but is soluble in acids. Lead borate is toxic. It is used in the ceramic and porcelain industries and in electroforming.

Lead carbonates are colourless crystals or white powdery substances that become yellowish or brownish upon aging as the result of the action of hydrogen sulphide. They are only slightly soluble in water and are able to form protective coatings on metallic lead articles. They are, however, soluble in acids and alkalies, except for ammonia and those acids with which leads forms slightly soluble compounds. Lead carbonate decomposes above 315°C, forming basic carbonates initially and lead monoxide at higher temperatures.

Lead carbonate is produced by reacting an aqueous solution of lead acetate with (carbon dioxide-containing) air or carbon dioxide gas, or also with ammonium carbonate or soda.

Basic lead carbonates (white lead) are produced by precipitation in heat or thermal decomposition of lead carbonate or through the direct action of acetic acid vapours and carbon dioxide (from a coke fire) on metallic lead.

White lead is used primarily as a pigment in the production of paints, cements and ceramic glazes. Accordingly, waste occurs in the form of paint residues as well as when buildings are renovated or torn down.

Lead chloride occurs in the form of white, silky crystals, as a white powder or as a horn-like substance ("horn lead"). It is slightly to very slightly soluble in water, somewhat soluble in dilute hydrochloric acid, quite soluble in ammonium solutions and glycerine. Lead chloride is toxic.

It is produced by reacting hydrochloric acid with lead oxide, lead carbonate or lead(II)solutions.

Lead chromate - see "Chrome Compounds"

Lead nitrates are colourless salts that are highly soluble in water, and even dissolve in alkalies and acids, except for those acids with which lead forms slightly soluble compounds. Lead nitrate is toxic. It decomposes above 470°C, releasing oxygen and forming basic nitrites initially and lead monoxide at higher temperatures. Lead nitrate is produced by reacting lead, lead shot, lead oxide, lead carbonate and other lead-containing residues with nitric acid. It is employed as an oxidizer in match stick heads and special explosive mixtures, and as a mordant for dyeing and printing textiles.

Lead(II)oxide (litharge) in its natural state is a red, crystalline flake (lithargite) or yellow lump material (massicot); when ground, it yields a correspondingly coloured powder. It is virtually insoluble in water, but because of its amphoteric nature is soluble in alkalies and acids, except for those with which lead forms slightly soluble compounds. Lime mortar and cement are also capable of dissolving lead oxide. Lead oxide is toxic.

It is one of the most important industrial lead compounds and is produced on a technical scale by oxidizing molten lead with air. The major application is in the fabrication of storage batteries and as a starting material for many other lead compounds, including ceramic glazes, as a drying agent in paints and to convert mercaptans to disulphides in oil refining.

Lead (II,IV) oxide (red lead) is a luminous red powder. Upon heating, it darkens; upon cooling, the colour returns. It turns black (lead sulphide) upon reaction with hydrogen sulphide or dissolved sulphide. It is virtually insoluble in water, soluble in hydrochloric acid and acetic acid, and noticeably soluble in citric acid (Lit. 17).

Lead(II,IV)oxide is toxic. It is produced by oxidizing lead monoxide or finely divided lead with air at 400° - 500°C, the product containing about 10% PbO in addition to approximately 90% Pb_3O_4. Mixed with linseed oil or alkyd resins, red lead is used as a rust-preventing paint for iron and steel, in the production of cements and glazes, as an additive to the composition of match stick heads and nonsaponifiable binders such as chlorinated rubber and epoxy resin.

Lead sulphate occurs as colourless crystals or as a white powder. It is virtually insoluble in water, and somewhat more soluble in concentrated strong acids (hydrochloric acid, nitric acid, sulphuric acid, not hydrofluoric acid) and in ammonium salt solutions.

Lead sulphate itself is hardly used technically, but occurs as a waste product. It is used as a thinner for lead chromates and as a substrate for colour lakes and coal-tar dyes. Basic lead sulphates, on the other hand, are of great technical significance, especially as heat and light stabilizers in vinyl resins, as painter's colour, for increasing the weight of linseed oil varnish, in batteries and in the production of red lead. Basic sulphates are generally produced through direct reaction of a lead oxide slurry with sulphuric acid to which a slight amount of acetic acid has been added.

Lead Compounds in the Synthetic-Resin Industry

Lead is superbly suited to stabilize vinyl resins against the action of heat and light. In addition to basic lead sulphate, a number of inorganic and organic lead compounds are used: lead cyanamide tetrabasic lead fumarate, tribasic lead maleate, dibasic lead hypophosphite hemihydrate, dibasic lead phthalate, lead stearate.

B. Organolead compounds

As an antiknock agent ("antiknock additive", "knock suppressor") for petrol engines, tetraalkyllead compounds of the type R_4Pb are added to the fuel, specifically tetraethyllead or tetramethyllead or a mixture of the two (TMEL). These are colourless, oily liquids that are heavier than water and insoluble in it. Their odour is unpleasantly sweet. They are miscible with other organic solvents besides petrol. Because of their solubility in fats and oils, they are quickly resorbed by the organism, even through the skin, and are thus particularly toxic. They react with most inorganic acids to form derivative compounds. They are resistant to air, moisture and moderate heat. They decompose slowly when exposed to light and temperatures of about 100°C, and are rapidly oxidized by air above 100°C. Production on a technical scale generally starts with lead alloys that are reacted with organic halides or esters. Organolead wastes occur primarily as dilute aqueous mixtures from the production process and as components of the sludge and coating deposited in storage and mixing equipment of plants and refineries.

Waste Treatment

In view of the economic importance of lead and its latent danger, it is desirable that lead residues be routed to a recovery plant to a great extent. In the case of scrap metal, economic recovery depends mainly on whether this scrap metal consists of pure or almost pure lead. Most scrap metal is usually remelted in blast furnaces constructed for the processing of lead as a first product, and the amount as well as the kind of metallic impurities decide whether such scrap metal can be tolerated with regard to the purity of the product. Waste gases produced during the metallurgical process are cooled by mixing them with air and then filtered, in conjunction with other equipment (e.g. a cyclone), through a fabric bag as dust collector.

Treatment with nitric acid to produce lead nitrate and subsequent precipitation of lead sulphide by introducing hydrogen sulphide into the lead nitrate solution is suitable as a standard method for recovering lead from impure residues and various lead compounds. The filtered lead sulphide can then be directed to the recovery plant.

Where lead and lead compounds occur in small, distributed amounts after use, disposal along with refuse and inert waste will be safe in most cases, in particular when metallic lead, lead carbonates, sulphate or sulphide are involved, i.e. compounds also found in naturally occurring minerals. It should nevertheless be pointed out in a precautionary sense that even these compounds are not insoluble. Lead sulphide is very slightly soluble in water, but 124 mg/l nevertheless dissolve at 20°C in pure water and even more in acidic solutions.

On the other hand, production-specific residues containing lead compounds in larger amounts, e.g. paint or organolead-containing sludges, should only be disposed of in special dumps, perhaps after a preliminary treatment or after special precautionary measures have been taken. An attempt must once again be made to convert the lead into the least soluble inorganic compounds possible and not to mix it with reactive waste that promotes mobilization of the lead.

Literature

1) Sorbe, G.: Gefährliche Arbeitsstoffe in Labor und Betrieb. 2nd completely revised edition, Umschau Publishing Co., Frankfurt/Main 1974.

2) Braun, W. and Döhnhardt, A.: Vergiftungsregister, Haushalts-und Laborchemikalien etc., Georg Thieme Publishing Co., Stuttgart 1970.

3) Moeschlin, S.: Klinik und Therapie der Vergiftungen. 5th revised and expanded edition, Georg Thieme Publishing Co. Stuttgart, 1972.

4) Flury, F. and Zenik, F.: Schädliche Gase. Julius Springer Publishing Co., Berlin 1931 (reprinted in 1969).

5) Valentin, H. et al: Arbeitsmedizin. Georg Thieme Publishing Col, Stuttgart 1971.

6) Wagner, R. and Zerlett, G.: Berufskrankheiten der 7. BeKV. 2nd revised edition, W. Kohlhammer Publishing Co., Stuttgart 1973.

7) Gesundheitsschädliche Arbeitsstoffe. Kommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe der DFG/Commission for the Testing of Hazardous Substances of the German Association for the Advancement of Scientific Research. Verlag Chemie, Weinheim/ Bergstraße, 2nd edition 1973.

8) Eschragi, I.: Gehalt und Wirkung von Spurenelementen aus Siedlungsabfällen und deren Aufbereitungsprodukten unter besonderer Berücksichtigung der Toxikologie. Landesstelle für Gewässerkd. u. wasserwirtschaftl. Planung Baden-Württ., Karlsruhe, Oct. 1974.

9) Schlipköter, H.-W.: An Pflanzen zeigt sich die Gefahr. UMWELT Forschung, Gestaltung, Schutz, 2/1973, 12-14.

10) Water Quality Criteria Data Book, Vol. 2, Inorganic Chemical Pollution of Freshwater. EPA Report No. 18010 DPV 07/71, U.S. Environmental Protection Agency, Washington D.C., A.D. Little, Inc., July 1971.

11) McKee, J.E. and Wolf, H.E., eds.: Water Quality Criteria. 2nd ed. California State Water Resources Control Board, Public 3-A, 1963.

12) Pierse, R.R.: Some cases of interest met with in practice - chronic lead poisoning (in cows). Veterinary Rec., Vol. 50, p. 145.

13) Hygiene-Institute des Ruhrgebiets, Gelsenkirchen: Wirkungs-konzentration (gesundheits-) schädigender bzw. toxischer Stoffe in Wasser für niedere Wasserorganismen sowie kalt- und warmblütige Wirbeltiere einschließlich des Menschen bei oraler Aufnahem des Wassers oder Kontakt mit dem Wasser.
Condensed version of a literature and data compilation. Ministry for Food, Agriculture and Forests of the State of North Rhein-Wesphalia, Düsseldorf.

14) Ohio River Valley Water Sanitation Commission, Metal Finishing Industries Action Comm., Subcomm. on Toxicities, Rept. 3, 1950.

15) Umweltblei in Ullmanns Enyclopädie der technischen Chemie, 4th revised and expanded edition, Vol. 8, p. 581, Verlag Chemie, Weinheim/Bergstraße, 1974.

16) Olson, K.W. and Skogerboe, R.K.: Identification of soil lead compounds from automotive sources. Science and Technology, Vol. 9 (3), 227, 1974.

17) Klein, E., Gabriel, J. and Goldschmidt, E.: Probleme bei der Beseitigung industrieller Abfallstoffe. Zeitschrift Kommunalwirtschaft, 4/1972, 134-138.

ARSENIC Compounds

Arsenic hydride

Formula AsH_3

CAS no.

Synonyms Arsine

Appearance Colourless gas with an unpleasant garlic odour

Melting point	$-116^{\circ}C$
Boiling point	$-55^{\circ}C$
Vapour pressure	
Density	1.6 g/ml at $-64^{\circ}C$ (liquid)
Vapour density ratio (air = 1)	2.695 (3.48 kg/m^3 (STP))
Solubility in water	200 mg/l, decomposes
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	2 mg/kg
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
	0.2							

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group

Remarks extremely toxic

1 mg/m^3 ≙ 0.313 ppm

1 ppm ≙ 2.81 mg/m^3

Description of Material

Arsenic hydride is a colourless, flammable, slightly water-soluble gas that is extremely toxic. It is released when dilute hydrochloric acid reacts with sodium arsenide. In pure form, arsenic hydride is odourless; in general, it smells like garlic because of impurities.

Hazards to Man

Intake of arsenic hydride occurs via the lungs exclusively. While the garlic smell is a warning, higher concentrations are no longer perceived as the result of paralysis of the olfactory nerves (Lit. 1). A few breaths (30 - 50 ml) of concentrated arsenic hydride are fatal immediately, 700 mg/m^3 = 250 ppm requiring one-half to one hour (Lit. 2). Even 140 mg/m^3 = 50 ppm are very toxic (Lit. 3). According to Lehmann (Lit. 4), even 50 mg/m^3 = 15.8 ppm are fatal in one-half to one hour. The MAK value is 0.14 mg/m^3 = 0.05 ppm.

Symptoms of acute poisoning do not develop until after a few hours (depending on the severity of the poisoning) and begin with general discomfort, sensation of cold in the hands and feet, headaches, difficulty in breathing and vomiting. Since arsenic hydride, as a distinct blood poison, destroys the red blood corpuscles, the urine turns red-violet, and later the skin as well. The products of the destruction block the kidneys and produce severe kidney damage, which may be fatal. Concerning the immediate aid that is necessary, the doctor should know that arsenic hydride and not arsenic poisoning is involved.

Chronic arsenic hydride poisoning is characterized by the identical symptoms, but they are less pronounced and are masked by the symptoms of a chronic arsenic poisoning.

Arsenic hydride poisonings are occupational diseases that must be reported.

Rooms in which arsenic hydride may form must be well ventilated; ferrosilicon stores should be kept dry. Arsenic hydride is highly inflammable and mixed with air or water explodes when ignited.

Hazards to the Environment

Arsenic hydride dissolves somewhat in water, simultaneously decomposing partially, so that arsenic hydride does not represent any specific burden on the environment. The toxicity range for short-term exposure is thus the same as that for arsenic compounds (4 - 9 mg/l for lower water organisms, 1 - 23 mg/l for fish).

Dogs and cats are about equally sensitive to arsenic hydride. The lethal dose is about 100 mg/m^3 for three hours' exposure (Lit. 5). In frogs only ten times this level leads to death (Lit. 6).

Production and Use/Waste Formation

Arsenic hydride is used in the electrical industry as a doping gas to manufacture semiconductors. Usually, however, the gas is a highly undesirable byproduct. It is formed as an impurity in hydrogen when inorganic acids react with metals, if at least one of the reactants contains arsenic. A few examples: pickling of metals in arsenic-containing hydrochloric or sulphuric acid, wet processing of ores, slags and metal speiss, dissolution of scrap zinc in acids (lithopone production), generation of hydrogen from zinc and hydrochloric acid in storage battery factories in the presence of arsenic-containing lead plates and decomposition of arsenic-contaminated calcium carbide or ferrosilicon. Further opportunities for poisoning exist in the production of vanadium steel, in sulphuric acid plants, when cleaning lead refineries if aluminium is introduced into the molten lead to remove arsenic and antimony.

Waste Treatment

Arsenic hydride is only problematical as "gaseous waste". Aqueous solutions of arsenic hydride decompose quickly and form other arsenic compounds, which are best precipitated as calcium arsenate and recycled or dumped (see "Calcium Arsenate").

Literature

1) Valentin, H.: Arbeitsmedizin, Thieme Publishing Co., Stuttgart (1971).

2) Jahr, G.: Dtsch. Gesundh.-Wes. 8 (1953) 208.

3) Taeger, H.: Die Klinik der entschädigungspflichtigen Berufskrankheiten, Springer, Berlin (1941) 103.

4) Lehmann, quoted in: Flury, F. / Zernick, F.: Schädliche Gase, J.-Springer Publishing Co., Berlin, (1931, reprinted in 1969).
Also contains additional literature data.

5) Dubitzki, Arch. f. Hyg. 73, 1 (1911).

6) Joachimoglu, Arch. f. exp. Pathol. u. Pharmak. 85, 32 (1919).

Arsenic trioxide

ARSENIC Compounds

Formula As_2O_3 **CAS no.** 1327533

Synonyms Arsenous oxide, arsenic(III)oxide

Appearance White powder or glassy mass

Melting point 313°C, sublimes above 193°C

Boiling point 457°C

Vapour pressure

Density 3.86 g/cm^3

Vapour density ratio (air = 1)

Solubility in water soluble to highly soluble (18.1 g/l at 20°C; 114 g/l at 100°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	1.4 - 5 mg/kg
Warm-blooded animals	20-138 mg/kg
Fish	10-100 mg/kg
Lower water organisms	2-4 mg/l

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
		0.5					I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
	0.04	0.05	0.05	0.05	0.1	

Remarks carcinogenic

Description of Material

Arsenic trioxide sublimes above 193°C(melting point 313°C). Depending on the temperature at which it condenses out of the gas phase, it has the appearance of a white, loose powder or colourless, glassy mass. The glassy form is more water-soluble than the crystalline one. The temperature dependence of the solubility in water is noticeably high.

Arsenic trioxide is the starting material for virtually all arsenic chemicals.

Hazards to Man

The toxic action of arsenic trioxide is so well known that it is considered the archetype of a poison far and wide. Except for the insoluble arsenic sulphides (realgar As_4S_4, auripigment As_2S_3), all arsenic compounds are toxic.

For arsenic trioxide the lethal dose is given as 0.1 g, but individual sensitivity fluctuates considerably. Moreover, a certain habituation may occur ("arsenic eaters"). After a latency period of a few hours, vomiting, diarrhea, general weakness, inflammation of the skin and collapse occur upon ingestion. Arsenic trioxide dust destroys tissue at places of contact (e.g. perforation of the nasal septum).

Chronic poisoning is characterized by symmetric pigmentation of individual sections of the body, persistent coughing, gastric and intestinal disorders and a gradual severe deterioration of physical and mental capabilities. Not all of the symptoms need be pronounced (Lit. 1).

Arsenic is eliminated by the body slowly. Repeated intake thus presents the danger of accumulation. It has been proven that arsenic produces cancer (lung and/or skin cancer) (Lit. 2, 3, 4).

Sicknesses caused by arsenic and arsenic compounds are considered occupational diseases (Lit. 5).

Hazards to the Environment

The literature data for lethal arsenic doses for animals and plants show a great deal of scatter; 2 - 4 mg/l kill all higher water plants and most lower water organisms, while 1 - 23 mg/l are given as the range for acute toxicity for short-term exposure in the case of fish. Mammals and man are more sensitive to arsenic than fish (Lit. 6). Arsenic accumulates in the flesh of a few edible mussels (Lit. 7). Drinking water cannot contain more than 0.04 mg As/l (Lit. 8).

Arsenic trioxide has been used as a defoliant and pesticide. Today the use of arsenic-containing products in agriculture is forbidden in the Federal Republic of Germany but not in the USA (Lit. 9).

Production and Use/Waste Formation

Arsenic trioxide is produced primarily as a byproduct during the metallurgical processing of ores which, in addition to arsenic, contain copper, silver, gold, lead, zinc, cadmium, nickel and cobalt. Arsenic trioxide, which is deposited in condensation chambers, is formed during roasting.

The glass-making industry uses arsenic trioxide as a decolourizing and refining agent. It is further used to prepare arsenic and arsenic compounds.

Arsenic-containing waste in the form of sludge or air-borne dust occurs during the metallurgical processing of arsenic-containing ores. The exhaust gases from these metallurgical plants also contain arsenic trioxide. The sulphur dioxide produced during pyrite roasting contains arsenic trioxide, which must be removed completely before further processing of the sulphur dioxide to yield sulphuric acid is possible.

Arsenic trioxide is further emitted during the burning of coal, which usually contains traces of arsenic (0.8 - 16 g/t). The highest concentration measured to date in the atmosphere was 1.4 mg As/l (Lit. 10).

Waste Treatment

To convert the gas-cleaning residues obtained during the metallurgical processing of arsenic-containing ores into a portable and less water-soluble form, the metals are precipitated as hydroxides by using an excess of lime water, and the arsenic is precipitated as calcium arsenate and calcium arsenite. This "arsenic sludge" is recycled, on the one hand, in order not to loose the valuable metals, and on the other, in order to reduce the problem of arsenic sludge disposal.

Arsenic trioxide is removed from waste gases by means of electrostatic separators (efficiency 70 - 90%) or bag filters (efficiency up to 99%). Bag filters, however, require twice to three times as much energy as electrostatic separators.

The following storage possibilities are available today for arsenic residues that cannot be recycled immediately or at all:

- Special dumps sealed against the penetration of ground water, surface water and rain water;
- Galleries in abandoned salt mines;
- Concrete silos.

Literature

1) Moeschlin, Sven: Klinik und Therapie der Vergiftungen, 5th edition, Thieme Publishing Co., Stuttgart 1972.

2) "Health Hazards of the Human Environment", edited by 100 specialists in 15 countries, Geneva, World Health Organization 1972.

3) Deutsche Forschungsgemeinschaft (German Society for the Advancement of Scientific Research), Report X of the Commission for the Testing of Hazardous Substances dated 14 June 1974, Maximale Arbeitsplatzkonzentrationen 1974 (MAK/Lower Toxic Limits).

4) Neumüller, O.A., Römpps Chemie-Lexikon, 7th edition, Franck'sche Verlagshandlung, Stuttgart 1972.

5) Wagner/Zerlett: Berufskrankheiten der 7. BekV, Kohlhammer Publishing Co., Cologne (1973).

6) Gelsenkirchener Dokumentation, Hygiene-Institut des Ruhrgebietes, Gelsenkirchen (1973).

7) Eisler, R.: "Annotated Bibliography on Biological Effects of Metals in Aquatic Environments", EPA, Ecological Research Series, EPA-R3-70-007 February 1973.

8) Bundesgesetzblatt I, 16, dated 15 February 1975: Verordnung über Trink- und Brauchwasser für Lebensmittelbetriebe.

9) Bundesgesetzblatt I, 55, dated 1 June 1974: Verordnung zur Neufassung der Verordnung über Anwendungsverbote und -beschränkungen für Pflanzenschutzmittel.

10) Sullivan, J.R.: Air pollution aspects of arsenic and its compounds. Report prepared for the National Air Pollution Control Administration by Litton Systems, Inc., Bethesda, Maryland under contract No. PH 22-68-25. Government Printing Office, 1969.

Calcium arsenate

Formula $Ca_3(AsO_4)_2$ **CAS no.** 7788441

Synonyms Arsenate of calcium,

Appearance White powder

Melting point	1455°C
Boiling point	
Vapour pressure	
Density	3.62 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	very slightly soluble (0.14 g/l at 20°C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	2 mg/kg
Warm-blooded animals	15 mg/kg
Fish	1 - 23 mg/l
Lower water organisms	4 - 9 mg/l

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		0.5					I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
	0.04	0.05	0.05	0.05	0.1	

Remarks carcinogenic

Description of Material

Calcium arsenate is a white, toxic powder that is very slightly water-soluble. Technical calcium arsenate or "arsenic sludge" (see below) contains in addition secondary calcium arsenate (synonym: acidic calcium arsenate) $CaHAsO_4 \cdot 3H_2O$ and basic salts such as $Ca_5(AsO_3)_2$.

Hazards to Man

In spite of its very poor solubility at pH 7, calcium arsenate represents a hazard to man, since the solubility increases greatly in an acidic environment. The toxicity range for short-term exposure is 5 - 50 mg/kg, which corresponds to 0.3 - 3.5 g (Lit. 1). See the sheet "Arsenic Trioxide" for symptoms of acute or chronic arsenic poisoning.

Hazards to the Environment

More important than isolated consideration of the toxicity of calcium arsenate is the toxicity of the arsenic sludge with its various arsenic components. When exposed to high temperatures, moisture and atmospheric carbon dioxide, neutral calcium arsenate reacts to form secondary calcium arsenate. Its solubility is about 25 times greater. When the sludge is improperly disposed of, arsenic concentrations that are considerably above the permissible TWVO value of 0.04 mg As/l (Lit. 3) can occur in ground and surface water (Lit. 2, 4).

According to reference 1, the toxicity ranges for short-term exposure are 20 - 100 mg/kg for warm-blooded animals and 45 - 96 mg/l (mg of calcium arsenate) for fish. A toxicity threshold of 9.2 mg of calcium arsenite/l has been established (Lit. 5) for the small crustacean "Daphnia magna".

Production and Use/Waste Formation

Using lime water containing iron, calcium arsenate is precipitated from arsenic-containing solutions that are produced in the extraction of copper, lead, silver, gold, cadmium, zinc, cobalt and nickel. The precipitate contains calcium arsenate, calcium arsenite, a few other arsenic salts and metal hydroxides, and forms the above-mentioned arsenic sludge, part of which is processed and part of which is disposed of. Of all arsenic compounds, only calcium arsenate is relevant in terms of the economics of waste management, since it is the only slightly soluble arsenic compound that occurs as a final product in a number of processes.

Waste Treatment

Arsenic sludge is either recycled or dumped (see also the sheet "Arsenic Trioxide").

Proper temporary or final disposal is possible

- in special dumps that are protected against the penetration of ground water, surface and rain water;
- in galleries of abandoned salt mines;
- in special concrete silos.

In any case, the sludge must be dewatered beforehand until it is compact.

Literature

1) Gelsenkirchener Dokumentation, Hygiene-Institut des Ruhrgebietes, Gelsenkirchen (1973).

2) Rasenberger, Wagenknecht et al: Gutachtliche Stellungnahme zur Frage der Auswirkungen der Ablagerungen arsenhaltiger Schlämme aus der Nievenheimer Zinkhütte auf Grund- und Oberflächenwässer unter besonderer Berücksichtigung hygienischer Gesichtspunkte. Institut für Wasser-, Boden- und Lufthygiene des Bundesgesundheitsamtes, Berlin-Dahlem 1971.

3) Verordnung über Trinkwasser und über Brauchwasser für Lebensmittelbetriebe (Trinkwasserverordnung), Bundesgesetzblatt I, 16 February 1975.

4) Klein, E. et al: Probleme bei der Beseitigung industrieller Abfallstoffe, Zeitschrift "Kommunalwirtschaft" 4, 1972.

5) Anderson, B.G.: The toxicity thresholds of various sodium salts determinated by the use of Daphnia magna. Sew. Works Journ. 18 (1946).
Anderson, B.G.: The toxicity thresholds of various substances found in industrial as determinated by the use of Daphnia magna. Sew. Works Journ. 16 (1944).

Beryllium

Formula Be

CAS no. 7440417

Synonyms Glucinium

Appearance Silver-white, shiny, brittle metal

Melting point	1284°C
Boiling point	2472°C
Vapour pressure	
Density	1.85
Vapour density ratio (air = 1)	
Solubility in water	virtually insoluble
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	100 mg/l (Be dust)
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	**MAK**	**TLV**	**MIK**		**TA Luft**			
			1/2 h	**24h**	**IW_1**	**IW_2**	**KL_S**	**KL_G**
		0.02					I	

Water mg/l	**TwVO**	**PLWS**	**ENV. 140 (EEC)**			**VLWF Group**
			A_1	**A_2**	**A_3**	
		1				

Remarks carcinogenic

1 mg/m^3 ≙ 2.7 ppm

1 ppm ≙ 0.04 mg/m^3

Beryllium chloride

Formula $BeCl_2$

CAS no. 7787475

Synonyms

Appearance White, asbestos-like interlocked crystals

Melting point 416°C

Boiling point 520°C

Vapour pressure

Density 1.9 g/cm^3

Vapour density ratio (air = 1)

Solubility in water highly soluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals 86 mg/kg (rats)

Fish

Lower water organisms

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
							I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		1				

Remarks carcinogenic

Beryllium fluoride

Formula BeF_2 **CAS no.** 7787487

Synonyms none

Appearance Glassy, colourless mass of very small crystals, highly hygroscopic

Melting point sublimes above 800°C

Boiling point

Vapour pressure

Density 1.98 g/cm^3

Vapour density ratio (air = 1)

Solubility in water very highly soluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
							I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLwF Group
		1				

Remarks carcinogenic

Beryllium hydroxide

Formula $Be(OH)_2$

CAS no. 13327327

Synonyms none

Appearance White, gygroscopic powder, soluble in acids and alkalies

Melting point is converted into BeO at 440°C

Boiling point

Vapour pressure

Density 1.92 g/cm^3

Vapour density ratio (air = 1)

Solubility in water virtually insoluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
							I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A$_1$	A$_2$	A$_3$	
		1				

Remarks carcinogenic

Beryllium oxide

Formula BeO

CAS no. 1304569

Synonyms Beryllia, glucina
Naturally occurring mineral: bromellite

Appearance White powder

Melting point	2410 - 2525°C
Boiling point	approx. 3900°C (estimated)
Vapour pressure	
Density	2.86 - 3.02 g/cm^3 (depending on method of preparation)
Vapour density ratio (air = 1)	
Solubility in water	virtually insoluble
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	**MAK**	**TLV**	**MIK 1/2 h**	**MIK 24h**	**TA Luft IW$_1$**	**TA Luft IW$_2$**	**TA Luft KL$_S$**	**TA Luft KL$_G$**
							I	

Water mg/l	**TwVO**	**PLWS**	**ENV. 140 (EEC) A$_1$**	**ENV. 140 (EEC) A$_2$**	**ENV. 140 (EEC) A$_3$**	**VL^{WF} Group**
		1				

Remarks carcinogenic

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Description of Material

Beryllium is a silver-white, shiny, hard metal. It is resistant to cold and warm water and cold oxidizing acids (e.g. nitric acid). It dissolves in dilute mineral acids (e.g. hydrochloric acid) and bases, forming hydrogen and a salt.

The mechanical properties (brittleness, ductility, tensile strength) depend to a great extent on the method of production and processing. Slight additions (other metals or beryllium oxide) also affect the properties to such a degree that technical beryllium qualities can be considered as alloys.

Beryllium is characterized by a low density at a useful strength, relatively high melting point, high specific heat and thermal conductivity, oxidation resistance and good transparency to X-rays.

Beryllium oxide is a white, water-insoluble, loose powder. It dissolves in concentrated sulfuric acid and is transformed into the acid-insoluble form upon heating.

Beryllium hydroxide ($Be(OH)_2 \cdot H_2O$) is obtained as a white, gelatinous precipitate upon adding bases to beryllium salt solutions. In the freshly precipitated state it is soluble in strong bases and acids (amphoteric). In boiling water, when drying or after standing for lengthy period of time, the hydroxide "ages" and becomes slightly soluble. It is converted into beryllium oxide upon heating to above 440°C.

Beryllium chloride is a white, deliquescent, crystalline substance which undergoes hydrolysis upon dissolving in water, giving off hydrogen chloride and heat. It is used to produce beryllium and for organic syntheses.

Beryllium fluoride is a highly soluble, white, hygroscopic mass. It occurs as an intermediate product in beryllium production. It is added to powdered welding fluxes for lightweight metals.

Hazards to Man

Beryllium and its salts are highly toxic. Oral poisonings are seldom but quite possible. The salts taste extremely sweet.

Vapours or dusts taken in via the respiratory tract are often more harmful. As with copper, zinc or cadmium, acute "metal-fume fever" (foundryman's fever), which either regresses without any consequences after 1 - 2 days or, however, which can be the preliminary stage of beryllium pneumonia, appears upon inhaling beryllium vapour. A symptom-free period lasting from days to months may pass between both forms of the illness. Beryllium-containing dusts can also cause pneumonia. The signs are difficulty in breathing, blue colouration of the lips, tortuous coughing and a great loss in weight.

The course of chronic pneumonia (beryllosis) caused by beryllium or beryllium compounds is similar. Long-term exposure to very low beryllium concentrations suffices to cause the illness (Lit. 1). It can last for years. In many cases beryllium poisonings are fatal.

Beryllium slivers or beryllium-containing dusts that penetrate the skin can produce poorly healing sores. These skin sores are some of the most severe known.

Not everyone who comes in contact with beryllium falls ill. In many individuals there is only a sensitization. An allergy mechanism is being discussed. According to A.J. Brestin (Lit. 2), exposure to 0.025 mg/m^3 for more than 30 minutes is already supposed to be harmful;

according to J.N. Sterner (Lit. 3), there were no cases of berylliosis over a period of 13 years in a beryllium alloy plant, although the on-the-job beryllium concentration was, on the average, 0.06 mg/m^3 in repeated, exact measurements.

In the USA the Environmental Protection Agency (EPA) has issued recommendations for maximum beryllium emissions: 0.025 mg Be/m^3 in 30 minutes are assumed safe (Lit. 5). This concentration is based on investigations of beryllium oxide, which forms during test running of rocket engines (beryllium powder as a fuel additive). The highly heated beryllium oxide discharged is "quite inert" and results in "few symptoms of illness" in rats and rabbits (Lit. 4).

Beryllium accumulates in the body and is eliminated only very slowly. In animal tests it causes (lung) cancer, while in man there are only reasons for suspicion to date. Accordingly, a MAK value (lower threshold limit) is not given.

Beryllium illnesses are occupational diseases that must be reported. The high hazard requires that careful occupational safety measures be taken. These include very good ventilation, fresh-air masks, showers, changing of clothes and regular medical checkups of the workers endangered.

Hazards to the Environment

In warm-blooded animals the harmful effects are chronic for 0.0001 mg/kg; 28.5 mg/l have no effect (Lit. 6), while 100 mg/l have a noticeable effect on fish (Lit. 7). In snails 28.5 mg/l produce no findings (Lit. 6). In general, plants tolerate 15 mg/l without a reduction in yield (Lit. 7). The beryllium concentration in water used for irrigation should not exceed 1 mg/l until more about the uptake of beryllium from the soil is known (Lit. 8).

Production and Use

Beryllium: the most important beryllium mineral worth mining is beryll ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$), which contains approx. 4% beryllium. In the USA bertrandite ($4BeO \cdot SiO_2 \cdot H_2O$), which contains approx. 0.3% beryllium is also mined. The ores are converted into an acid-soluble form by means of a decomposition process (thermal or with alkali) and processed in a number of intermediate steps to yield beryllium hydroxide ($Be(OH)_2$) and then further to beryllium chloride ($BeCl_2$) or beryllium fluoride (BeF_2). Crude beryllium is obtained by reducing with sodium or magnesium or through electrolysis of beryllium chloride. It is purified by means of vacuum melting and then ground to powder.

Cast beryllium components have poor mechanical properties. Ingots or preformed parts are thus manufactured powder metallurgically (hot pressing in graphite or steel moulds in vacuum furnaces). Unalloyed beryllium is used for X-ray windows, in nuclear engineering (favourable moderator and reflector properties for thermal neutrons) and - in powder form - as an additive to solid rocket fuels. The hardness, strength, insensitivity to temperature and corrosion resistance of copper, aluminium, nickel, cobalt and iron are increased tremendously through alloying with beryllium (example: nonsparking and nonmagnetic tools made of a copper-beryllium alloy). The alloy "Lockalloy", which is produced powder metallurgically and contains 38% aluminium, is used for the construction of aircraft, rockets and satellites.

Beryllium oxide is obtained by roasting beryllium hydroxide or other beryllium salts that occur as intermediate products in beryllium extraction. Chemically, it is extremely stable. The higher the calcination temperature, the more inert it is.

Beryllium oxide is used in the production of ceramic materials characterized by good electrical insulating properties and thermal conductivity. Examples of application include highly refractory devices, aircraft spark plugs and insulating material for radar tubes.

Waste Formation/Waste Treatment

Because of the high costs of beryllium production, beryllium producers and users attempt to keep waste to a minimum or recycle it into the fabrication process. This is also achieved to a high degree. Beryllium occurring in production and processing in the form of powder or chips as well as beryllium compounds (as intermediate products) are reused. Producers buy back scrap beryllium.

The emission of beryllium-containing dusts can be brought to a satisfactory value (on the average 0.01 g/m^3 over a time span of 30 days in the USA) through the use of filters and scrubbers (Lit. 9).

Liquid or solid waste with too low a beryllium concentration to warrant recovery is disposed of in special dumps. Prior to disposal, however, the beryllium compound involved must be converted into the relatively inert oxide (Lit. 10).

Literature

1) G.E. Meyer, H.J. Henning: DMIC - Report No. S - 29 (1970).

2) A.J. Prestin et al. Arch. Ind. Health 19, 596 (1959).

3) J.N. Sterner, M. Eisenbud: Arch. Ind. Hyg. 19, 596 (1959).

4) "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste, XII, 249 (1973).

5) Environmental Protection Agency. Background information - proposed national emission standards for hazardous air pollutants-asbestos, Be, Hg. Research Triangle Partk, North Carolina, Dec. 1971.

6) Gelsenkirchener Dokumentation, Hygiene-Institut des Ruhrgebietes, Gelsenkirchen, 1973.

7) "Control of Spillage of Hazardous Polluting Substances", Battelle Memorial Institute, Federal Water Quality Administration, Report 15090 FO2 10/70 November 1970.

8) Water Quality Criteria, Report of National Technical Advisory Committee to the Secretary of the Interior, Federal Water Pollution Control Administration 1 April 1968.

9) "Report to Congress on Hazardous Waste Disposal", U.S. EPA 30 June 1973.

10) Ottinger, R.S. et al: "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 volumes, issued for the EPA, TRW Systems Group, PB 224579, Set/As, 1 February 1973.

Antimony

Formula Sb

CAS no. 7440360

Synonyms

Appearance Silver-white metal

Melting point 630°C

Boiling point 1322 - 1440°C (depending on the method of measurement

Vapour pressure

Density 6.69 g/cm^3

Vapour density ratio (air = 1)

Solubility in water insoluble

Flash point

Ignition temperature approx. 750°C

Inflammable mixture

Toxicity range for short-term exposure:

Man	1 - 2 mg/kg
Warm-blooded animals	100 mg/kg
Fish	
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.5	0.5					II	

Water mg/l	TWVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.05				

Remarks

284<

Antimony hydride

Formula SbH_3

CAS no.

Synonyms Stibine

Appearance Colourless, foul-smelling gas

Melting point	-90°C
Boiling point	-18°C
Vapour pressure	
Density	5.3 g/cm^3
Vapour density ratic (air = 1)	4.36 at 15°C
Solubility in water	soluble (4.1 g/l at 0°C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man (fatal in 1 hour)	500 mg/m^3
Warm-blooded animals	200 mg/m^3
Fish	
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	**MAK**	**TLV**	**MIK** 1/2 h	24h	**TA Luft** IW_1	IW_2	KL_S	KL_G
	0.5	0.5						

Water mg/l	**TwVO**	**PLWS**	**ENV. 140 (EEC)** A_1	A_2	A_3	**VLWF Group**

Remarks extremely toxic

285<

1 mg/m^3 ≙ 0.2 ppm
1 ppm ≙ 5 mg/m^3

Antimony trioxide

Formula Sb_2O_3

CAS no. 1309644

Synonyms Antimony(III)oxide, antimony bloom, valentinite, white antimony

Appearance White powder

Melting point	655°C
Boiling point	1456°C
Vapour pressure	
Density	5.2 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	virtually insoluble (0.014 g/l at 30°C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	20 mg/kg
Warm-blooded animals	80 mg/l
Fish	
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	**MAK**	**TLV**	**MIK** 1/2 h	24h	**TA Luft** IW_1	IW_2	KL_S	KL_G
		0.5					II	

Water mg/l	**TwVO**	**PLWS**	**ENV. 140 (EEC)** A_1	A_2	A_3	**VLWF** Group
		0.05				

Remarks

Description of Material

Antimony is a silver-white, brittle metal which in compact form at room temperature does not change in air. The molten metal ignites upon exposure to air and burns to form antimony oxides.

Like water, antimony is one of the few substances that expands upon solidifying (suitable for printing type).

Antimony trioxide is a white, odourless, water-insoluble powder. It dissolves in acids and alkalies, forming a salt.

Antimony hydride is a colourless gas. Its odour is musty and somewhat reminiscent of hydrogen sulphide, but is completely different from that of arsenic hydride or of phosphorous hydride. Soluble in water, alcohol, ether and benzene.

Antimony hydride decomposes in air at normal temperatures (autocatalysis).

Hazards to Man

The following symptoms may appear at an antimony concentration of 4.7 mg/m^3: eczema-like skin eruptions, inflammation of the mucous membranes, gastric, intestinal and nervous disorders. In one case of death, the fatal dose was 97 mg (Lit. 1, 2). Other authors (Lit. 3) claim that antimony metal is not toxic at all. The poisoning effect is supposed to be the result of accompanying alloy components (arsenic, lead).

Finely divided antimony is explosive. It reacts spontaneously and vigorously with free halogens, giving a flame.

Inhalation of 3 - 5 mg/m^3 of antimony trioxide dust or vapour over a period of five working months causes severe irritation of the mucous membranes (Lit. 4).

If they reach the blood, antimony compounds are just as toxic as the related arsenic compounds. Antimony poisonings due to ingestion, however, are seldom, since antimony salts pass through the stomach and intestinal walls only with difficulty and cause in addition severe nausea.

Antimony hydride forms (as does arsenic hydride) when an antimony-containing alloy comes in contact with acid. Antimony hydride (SbH_3) is considerably more toxic than all other antimony compounds and can be compared roughly with arsenic hydride (AsH_3). After inhalation for one hour, 200 mg/m^3 ≙ 40 ppm may be fatal (Lit. 3). Acute poisonings cause headaches, nausea, weak, irregular breathing and all the consequences of severe haemolysis (red coloured urine, kidney and liver damage). As antimony hydride decomposes relatively rapidly, the hazard is normally not great. Possible sources should, however, be well ventilated. If antimony hydride forms in quantities that may be toxic, all measures described for arsenic hydride should be taken. Antimony hydride is explosive.

Hazards to the Environment

Environmental degradation due to antimony compounds has not been observed to date. The following results from experiments on animals are available:

Antimony metal: The LD_{50} for rats is 100 mg/kg (Lit. 5, 6).
Antimony trioxide: Toxicity range for short-term exposure: 20 mg/kg for warm-blooded animals, 80 mg/l for fish (Lit. 7).
Antimony hydride: Exposure to 0.0005 mg/m^3 for 100 minutes results in death in mice (Lit. 8).

Production and Use/Waste Formation

The most important antimony ore is antimonite (Sb_2S_3). In rich ores, (<50% gangue) the antimony sulphide is extracted by melting ("liquation") and it is processed using a dry method (see below). Oxide or sulphide carried along by the combustion gases is trapped in filters and returned to the process. The liquation residues, which contain about 10% antimony, are processed to yield antimony trioxide.

Poor sulphidic or oxidic antimony ores are processed to yield crude antimony by means of the reaction roasting or reduction roasting methods. The slag produced still contains approx. 1% antimony.

If the ores contain gold or silver, dissolution in acidic or alkaline media with subsequent electrolysis or cementation may be more economical. After dearsenication, the antimony is 99.7% pure. Waste water or residual liquids occur in all wet processes and in electrolysis anode sludges as well.

Copper and lead ores often contain considerable amounts of antimony. Separation of the antimony in one concentrate is not possible with the pyrometallurgical processes involved. It is to be found in air-borne dust, dross, speiss, slag and final product, especially in the case of lead.

Scrap antimony, which always contains rather large amounts of lead, is treated like lead ore. The hard lead produced is either diluted with pure lead to yield a marketable lead-antimony alloy or is electrolytically refined.

Antimony produced using one of the listed methods is more or less impure and also contains arsenic, in addition to other metals. To remove these impurities, especially arsenic, the metal is fused with caustic soda. Air is blown into the metal-caustic soda bath for a long period of time, and the impurities form a slag.

Antimony that is 99.99% pure for use as a solvent for high-purity silicon is obtained by subliming an antimony-manganese-aluminium alloy.

A small fraction of the antimony produced is used to make antimony compounds. Roughly 95% of the antimony produced is alloyed with lead and/or tin, since it hardens these metals (bearing metal, type metal, britannia metal). The alloys are used in the manufacture of lead storage batteries, printing type, sheet metal, pipes and tubes.

Ultrahigh-purity antimony is used in semiconductor engineering.

Antimony trioxide is obtained by roasting antimony sulphide, by hydrolyzing antimony sulphide with superheated steam or by burning antimony in air or oxygen. Antimony trioxide is used in the production of other antimony compounds, in the glass, ceramic and paint industries as well as to make fabrics and plastics fireproof. Problems in the formation of antimony wastes arise especially because of the low melting point and high volatility of antimony metal and because of the sublimability of antimony trioxide.

The emission in air is estimated to be 7.5 mg/m^3. Slags are stored at the site of production for occasional reprocessing (approx. 1% antimony content). Waste water, scrap, flue dusts, electrolysis sludge and electrolyte are recycled into production.

Antimony hydride is formed during the production of antimony trichloride, during the brown-finishing of steel and during the cleaning of type metal in sodium hydroxide solution. It hardly occurs as waste.

Waste Treatment

Antimony and antimony trioxide dusts are collected by means of bag filters and reused. Antimony-containing waste water is concentrated and reacted with sodium sulphide and charcoal in an electric furnace at a temperature of 1250°C to form sodium antimonate. No harmful waste gases are formed in this method. The product is reused in antimony production.

Literature

1) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 volumes, issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973.

2) McKee, J.E. and Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

3) Hamilton, A. et al: Industrial Toxicology, 2nd edition, Thieme Publishing Co., Leipzig 1947.

4) Renes, L., Arch. Ind. Hyg. Occup. Med. 7, 99 (1953).

5) Sax, N.I., Dangerous properties of industrial materials. 3rd ed., New York, Reinhold Publishing Company, 1968.

6) Christensen, H.E., Toxic substances; annual list, 1971. Rockville, Maryland, U.S. Department of Health, Education, and Welfare, Health Services and Mental Health Administration, National Institute for Occupational Safety and Health, 1971.

7) "Gelsenkirchener Dokumentation", Hygiene-Institut des Ruhrgebietes, Gelsenkirchen, 1973.

8) Stock et al, Ber. Dtsch. Chem. Ges. 37, 893 (1934).

Chromium(III)hydroxide

CHROMIUM Compounds

Formula $Cr_2O_3 \cdot x\,H_2O$

CAS no. 1308141

Synonyms Hydrated chromium(III)oxide

Appearance Bluish to grey-green, gelatinous

Melting point +)

Boiling point

Vapour pressure

Density

Vapour density ratio (air = 1)

Solubility in water virtually insoluble (13.7 mg/l)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	5 - 15 g/kg
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3 ++)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		1.0						

Water mg/l ++)	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
	0.05	0.05	0.05	0.05	0.05	

Remarks +) is converted into Cr_2O_3 upon heating (melting point 2435°C)

++) as total Cr

Chromium(VI)oxide

CHROMIUM Compounds

Formula CrO_3

CAS no. 133820

Synonyms Chromium trioxide, chromic anhydride

Appearance Dark red, needle-shaped crystals, hygroscopic

Melting point 197°C
Boiling point melt decomposes
Vapour pressure
Density 2.7 g/cm³
Vapour density ratio (air = 1)
Solubility in water very highly soluble (1660 g/l at 15°C)
Flash point
Ignition temperature
Inflammable mixture

Toxicity range for short-term exposure:

Man 50 - 500 mg/kg
Warm-blooded animals
Fish 200 - 500 mg/l
Lower water organisms 0.6 mg/l

Occupational safety - Danger symbols O + C

Safety guidelines

Air mg/m³ +)	**MAK**	**TLV**	**MIK**		**TA Luft**			
			1/2 h	**24h**	**IW_1**	**IW_2**	**KL_S**	**KL_G**
	0.1	0.1					I	

Water mg/l +)	**TwVO**	**PLWS**	**ENV. 140 (EEC)**			**VL^{WF} Group**
			A_1	**A_2**	**A_3**	
	0.05	0.05	0.05	0.05	0.05	

Remarks +) as total Cr

Basic chromium(III)sulphate

CHROMIUM Compounds

Formula $Cr(OH)SO_4$

CAS no. 12336957

Synonyms

Appearance Green powder or flakes

Melting point

Boiling point

Vapour pressure

Density

Vapour density ratio (air = 1)

Solubility in water highly soluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	0.5 - 5 g/kg
Warm-blooded animals	
Fish	1.2 - 200 mg/l
Lower water organisms	0.03-0.1 mg/l

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		0.5						

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	0.05	0.05	0.05	0.05	0.05	

Remarks +) as total Cr

294<

Lead chromate (VI) CHROMIUM Compounds

Formula $PbCrO_4$ **CAS no.** 7758976

Synonyms Chrome yellow; Cologne, Leipzig, Paris yellow; king's yellow, new yellow

Appearance Orange-yellow powder

Melting point 844°C
Boiling point melt decomposes
Vapour pressure
Density 6.1 g/cm^3
Vapour density ratio (air = 1)
Solubility in water virtually insoluble (0.06 mg/l at 25°C)
Flash point
Ignition temperature
Inflammable mixture

Toxicity range for short-term exposure:
Man
Warm-blooded animals
Fish
Lower water organisms

Occupational safety - Danger symbols Xn

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		0.1					I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
	0.05	0.05	0.05	0.05	0.05	

Remarks$^{+)}$ as total Cr (also as total Pb)

Potassium chromate(VI)

Formula K_2CrO_4 **CAS no.** 7789006

Synonyms Chromate of potassium

Appearance Yellow crystals

Melting point 975°C

Boiling point

Vapour pressure

Density 2.7 g/cm^3

Vapour density ratio (air = 1)

Solubility in water highly soluble (629 g/l at 20°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	
Fish	15 - 195 mg/l
Lower water organisms	0.3-0.7 mg/l

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
		0.1					I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group
	0.05	0.05	0.05	0.05	0.05	

Remarks +) as total Cr

Potassium dichromate(VI)

Formula $K_2Cr_2O_7$

CAS no. 7778509

Synonyms Potassium bichromate, dichromate of potassium

Appearance Orange-red powder or tabular crystals

Melting point 396°C

Boiling point melt decomposes above 500°C

Vapour pressure

Density 2.7 g/cm^3

Vapour density ratio (air = 1)

Solubility in water highly soluble (resembles K_2CrO_4)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols Xi

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		0.1					I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
	0.05	0.05	0.05	0.05	0.05	

Remarks +) as total Cr

Sodium chromate (VI)

CHROMIUM Compounds

Formula Na_2CrO_4

CAS no. 10588019

Synonyms

Appearance Yellow crystals

Melting point

Boiling point

Vapour pressure

Density 2.7 g/cm^3

Vapour density ratio (air = 1)

Solubility in water highly soluble (873 g/l at 30°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg
Warm-blooded animals	
Fish	15 - 195 mg/l
Lower water organisms	0.3-0.7 mg/l

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
		0.1					I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
	0.05	0.05	0.05	0.05	0.05	

Remarks +) as total Cr

Sodium dichromate (VI) dihydrate CHROMIUM Compounds

Formula $Na_2Cr_2O_7$ CAS no. 7775113

Synonyms Sodium bichromate

Appearance Orange-red crystals, hygroscopic

Melting point 357°C (dehydrates above 83°C)

Boiling point 400°C (decomposes)

Vapour pressure

Density 2.52 g/cm^3

Vapour density ratio (air = 1)

Solubility in water very highly soluble (1800 g/l at 20°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols Xi

Safety guidelines

Air mg/m^3 +)	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
		0.1					I	

Water mg/l +)	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
	0.05	0.05	0.05	0.05	0.05	

Remarks +) as total Cr

Zinc chromate (VI)

CHROMIUM Compounds

Formula $ZnCrO_4$

CAS no. 13530659

Synonyms Zinc yellow, chromate of zinc

Appearance Lemon-yellow powder

Melting point

Boiling point

Vapour pressure

Density 3.4 g/cm^3

Vapour density ratio (air = 1)

Solubility in water virtually insoluble

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3 +)	**MAK**	**TLV**	**MIK** 1/2 h	24h	**TA Luft** IW$_1$	IW$_2$	KL$_S$	KL$_G$
		0.1					I	

Water mg/l +)	**TwVO**	**PLWS**	**ENV. 140 (EEC)** A$_1$	A$_2$	A$_3$	**VLWF Group**
	0.05	0.05	0.05	0.05	0.05	

Remarks +) as total Cr

that may ultimately end in perforation of the nasal septum. Lesions and eczema (chromate eczema) appear on the skin. The skin sores heal poorly but are hardly painful. Allergic reactions appear.

The intake of chromic acid or soluble chromate through the mouth and stomach is usually prevented by the strongly biting, acidic taste. Repeated ingestion of small amounts, however, can result in inflammations of and lesions in the gastrointestinal tract. The probably fatal dose is set at 1 g. Acute symptoms include the vomiting of yellow-green and perhaps bloody clumps, nausea, abdominal pains, diarrhea, bloody urine and retention of urine.

Hazards to the Environment

The toxicity of chromium salts for organisms living in water fluctuates within wide limits, depending on the species, temperature, pH value, valence of the chromium and synergetic or antagonistic effects, especially the hardness of the water. Fish have a relatively good tolerance to Cr salts (up to 1 mg/l), lower life forms, however, are extremely sensitive. The degree of toxicity for lower water organisms and cold-blooded animals is greater than that for warm-blooded animals.

Description of Material / Production and Use / Waste Formation

Chromium(III)hydroxide is a water-rich, gelatenous, bluish to grey-green precipitate that forms during alkaline precipitation and the reducing treatment of chromium-containing industrial waste water, especially that from electroplating shops and tanneries. The optimum value for precipitation is pH 10, where the residual solubility of chromium(III) is 0.3 mg/l, while at pH 7 13.7 mg/l remain in solution (Lit. 8). The hydroxide, which is virtually insoluble between pH 6 and pH 11, is, however, soluble in acids and strong bases because of its amphoteric nature. Upon heating, chromium(III)hydroxide is easily transformed into chromium(III)oxide, Cr_2O_3, with the release of water. The oxide is also virtually insoluble in acids and alkalies.

Chromium trioxide (chromic acid) is dark red, crystalline, hygroscopic, very highly water-soluble, corrosive and very toxic. It is a strong oxidant and can react explosively with alcohol and other organic substances such as ether, anthracene and analine!

It is obtained from alkali chromate solution by precipitation with concentrated sulphuric acid and is used in dyeing and tanning, the ceramic and paper industries, for pickling, etching and electroplating of chromium onto metal surfaces, for anodizing of aluminium, for producing gas cleaning agents, for electric batteries, in the organics industry for oxidative bleaching of crude montan wax, as well as in the production of paints, dyes and explosives.

Basic chromium(III)sulphate is a green, water-soluble powder that is used extensively in leather tanning and working; 90% of all leather is chrome-tanned. In addition to chromium sulphate, chrome alum is also used.

Lead chromate (chrome yellow) is an orange-yellow powder. It is virtually insoluble in water but soluble in acids and alkalies. It is toxic.

Technical lead chromate is produced by reacting a lead salt solution with chromate or dichromate to which sulphuric acid or alkali sulphate has been added, leading to formation of a mixed crystal with lead sulphate. It is generally used as a pigment for paints, printing ink and artist's colours, as well as in the production of chrome yellow and chrome green. Chrome red (chrome cinnabar, derby red, Persian or Vienna red) is basic lead chromate, $PbO \cdot PbCrO_4$, and is likewise employed as a paint pigment as well as component in chrome orange.

Potassium chromate is yellow, crystalline, water-soluble and very toxic. It is produced by reacting sodium chromate with potassium chloride and is used in dyeing, textile printing, ink fabrication and in the production of lead chromate pigments.

Potassium dichromate is an orange-red powder or crystalline, water-soluble and very toxic. It is a strong oxidant and is capable of releasing chlorine gas from hydrochloric acid!

It is produced by reacting sodium dichromate with potassium chloride and is used in the production of lead chromate pigments, as an oxidant in the dye industry, as an active agent in wood preservatives as well as in electroforming, photography and photocopying.

Sodium chromate is yellow, crystalline, water-soluble and very toxic. It is produced technically as the primary chromate by oxidizing chrome iron ore in air, lime and soda, and serves as the starting material for the other chromates and chromium compounds.

Sodium chromate hydrates crystallize out of the solution at temperatures below 63°C and are used in pigment production, dyeing and tanning as well as in corrosion protection, especially in the petroleum industry.

Sodium dichromate is orange-red, crystalline, hygroscopic, water-soluble and very toxic. It is produced by reacting sodium chromate with concentrated sulphuric acid and crystallizes out of the solution as the dihydrate when the temperature is below 83°C. It is the technically most important compound of hexavalent chromium and is used in the production of chromic acid and potassium dichromate; the uses are the same as for potassium dichromate.

Zinc chromate hydrates (zinc yellow) are lemon-yellow to pure yellow powders, virtually insoluble in water but soluble in acids and are attacked by alkalies. Mixed with oil or phenolic resin varnishes, they serve as rust-preventing paints. They are further employed as pigments for linoleum and plastics.

Waste Formation

The galvanizing and metal processing industries are a major source of chromate waste. It is estimated that only 10 to 20% of the chromium used for metal finishing ends up in the chrome-plated product. Chromium-containing waste is produced during flushing and draining of cleaning, pickling and replating solutions. Unreacted chromates occur in the form of concentrates and semiconcentrates. In the textile industry chromate solutions are used to kill algae and prevent corrosion as well as to oxidize and produce colour-fast sulphur dyes for cotton fabrics. Chromium-containing waste water is produced during these processes.

Tanning consumes considerable amounts of sodium dichromate, which is converted to chromium(III)sulphate (basic). The bulk of tannery waste is this substance.

Pigment colours are mixed from chromate compounds of barium, lead, molybdenum and zinc. They are used extensively in the paint, printing ink and plastics industries.

Waste Treatment

Dissolved or soluble chromium compounds in which the chromium is more than trivalent, thus chromate waste above all, must be reduced chemically and precipitated as chromium(III)hydroxide. The precipitated sludges must be compacted by partial dewatering to enable disposal and prevent degradation of waters and ground water. Normal standards for the introduction of electroplating waste water into the sewerage system tolerate a maximum of 2 mg of chromium per litre of waste water, dissolved or undissolved (Lit. 9).

Where no central detoxification, neutralization, and sludge dewatering systems are available, these waste and waste water treatment measures must be taken in the plants. To this end, chromate-containing wastes, baths, eluates and semiconcentrates must be collected separately. Reduction to trivalent chromium is usually accomplished with the aid of sodium bisulphate in sulphuric acid solution (pH 2 - 3). Under certain circumstances, agents such as sulphur dioxide from waste gases or sulphite- containing liquids obtained from the scrubbing of waste gas, iron filings, brass or aluminium chips can be profitably used for reduction. The subsequent precipitation of the chromium is accomplished by alkalizing to pH 8 - 9; waste alkali solutions or alkaline treated waste water, e.g. from cyanide detoxification, can be used here. The sludge is usually dewatered through a process of sedimentation in settling basins, decanting and pressing of the thin sludge in chamber filter presses, insofar as it cannot be recycled. Depending on local conditions, the compacted sludge (residual water content 60 - 70%) is disposed of in single-purpose dumps approved for this purpose, dumps for special waste or refuse dumps.

Chromium-containing sludges or residues cannot be disposed of in incinerators, as the trivalent chromium is reoxidized to hexavalent chromium in the heat.

The reclamation of chromate from the sulphuric acid solutions of chromium(III)sulphate produced in dye factories is of some technical importance; this is accomplished electrolytically through anodic oxidation.

Literature

1) Sorbe, G.: Gefährliche Arbeitsstoffe in Labor und Betrieb. 2nd completely revised edition, Umschau Publishing Co., Frankfurt/Main 1974.

2) Braun, W. and Dönhardt, A.: Vergiftungsregister, Haushalts- und Laborchemikalien etc. Georg Thieme Publishing Co., Stuttgart, 1970.

3) Moeschlin, S.: Klinik und Therapie der Vergiftungen. 5th revised and expanded edition, Georg Thieme Publishing Co., Stuttgart, 1972

4) Flury, F. and Zenik, F.: Schädliche Gase. Julius Springer Publishing Co., Berlin 1931 (reprinted in 1969).

5) Valentin, H. et al.: Arbeitsmedizin. Georg Thieme Publishing Co., Stuttgart 1971.

6) Wagner, R. and Zerlett, G.: Berufskrankheiten der 7. BeKV. 2nd revised edition, W. Kohlhammer Publishing Co., Stuttgart 1973.

7) Gesundheitsschädliche Arbeitsstoffe. Kommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe der DFG. Verlag Chemie, Weinheim/Bergstraße, 2nd edition 1973.

8) Schlaitzer, J.: Geordnete Ablagerung schlammiger Abfälle. Müll und Abfall 2/1971, 43 - 45.

9) Bucksteeg, W.: Beseitigung anorganisher Schmutzstoffe - Forderungen und ihre Erfüllung. gwf - Wasser - Abwasser, Vol. 108, 1967, 962 - 965 and 1018 - 1021.

Selenium

SELENIUM and SELENIUM Compounds

Formula Se

CAS no. 7782492

Synonyms none

Appearance
Exists in various modifications:
Red: crystalline or amorphous
Black: glassy or amorphous
Grey: crystalline, metallic

Melting point	217°C (grey modification)
Boiling point	685°C "
Vapour pressure	
Density	4.79 g/cm^3 (grey modification)
Vapour density ratio (air = 1)	
Solubility in water	virtually insoluble
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	4 g no effect 0.01 mg/l chron.
Warm-blooded animals	
Fish	2 mg/l
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW$_1$	IW$_2$	KL$_S$	KL$_G$
	0.1	0.2					I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF
			A$_1$	A$_2$	A$_3$	Group
	0.008	0.01	0.01	0.01	0.01	

Remarks carcinogenic action is being discussed

SELENIUM

Description of Material

Selenium occurs in nonmetallic (red or black, crystalline, amorphous or glassy-amorphous) modifications and in a grey-black hexagonal crystalline form. The latter has a metallic appearance and to a certain extent metallic properties as well. While its dark conductivity cannot be compared with that of actual metals, it does show pronounced photo-conductivity.

Upon being heated in air, selenium burns to form selenium dioxide. Selenium reacts with many metals to form selenides, which generate selenium hydride upon contact with dilute acids. Selenium is not attacked by non-oxidizing acids, but it does dissolve in concentrated sulphuric acid upon heating, giving a green colour.

Selenium forms the same compounds as does sulphur; selenium is thus di-, tetra- and hexavalent. In aqueous solutions selenium is probably tetravalent (selenite) or hexavalent (selenate). An unambiguous analytical method of differentiating between these two must still be found.

Hazards to Man

As almost all metals, sufficiently finely divided selenium powder can also explode in air. The very toxic selenium hydride forms when selenides, which are produced in the reaction of selenium with metals, come in contact with water vapour.

Pure selenium taken orally is supposed to be harmless (Lit. 1). Elemental selenium is not contained in an American list of toxic substances (Lit. 2; 1971). Inhaled as a vapour or dust, however, selenium is toxic (Lit. 3) and causes severe irritation of the mucous membranes and respiratory tract, a burning feeling and dryness in the nose and gullet, and a metallic taste in the mouth. In addition, coughing and signs of pulmonary edema may develop (Lit. 4).

On the skin, selenium may cause blisters and other skin sores (Lit. 5).

Selenium compounds are a number of times more toxic than elemental selenium, the extent of the harmful effects depending above all on the solubility of the selenium compounds. The most toxic selenium compounds are selenium hydride (it can occur in metallurgy and the cement industry, and, as a poison attacking the lungs and mucous membranes, cause "selenium sniffles" and even pulmonary edema) and certain organic selenium compounds such as methyl and ethyl selenide as well as aromatic selenium compounds (Lit. 6). Selenium poisonings are characterized usually by a typical, intensive garlic odour of the breath and perspiration (this odour may last for months). Symptoms are frontal headaches, extreme paleness, nervousness, a heavily coated tongue, depressive mood, skin inflammations, stomach and intestinal disorders and/or damage to the lungs, liver and other internal organs.

In the past few years, the possibility that selenium is carcinogenic has moved into the foreground of considerations (Lit. 6, 7, 8).

Hazards to the Environment

The classical selenium poisoning in animals, the "alkali disease", was already observed in the middle of the previous century in army horses in America. For a long time the high alkali content of the water there was held to be the cause of the sickness (thus the name); selenium was not recognized as the cause until about 1930. In addition to the chronic ("alkali disease") form, the acute form is known as "blind staggers".

SELENIUM

Such selenium-induced illnesses can be observed especially in areas with pyritous soils, on which selenium-concentrating plants grow (Lit. 9). In this case, the selenium is present as an organic compound. Organic selenium compounds are more toxic than inorganic ones.

A compilation of selenium doses harmful to various house pets can be found in Lit. 10.

In warm-blooded vertebrates, as in man, certain sodium selenite levels in drinking water during the period of tooth development result in the increased occurrence of caries (Lit. 11).

It should also be noted, however, that in small amounts selenium promotes physiological functions, i.e. is a vital trace element.

In the form of sodium selenite, selenium concentrations of 4.6 mg Se/l are fatal to goldfish within 98 to 144 hours. Lower concentrations of 2 mg Se/l have toxic effects on goldfish after 8 days; after a longer exposure (18 - 46 days) death occurs (Lit. 12).

Certain plants can, if they grow on soils that are especially rich in selenium (pyritous soils), concentrate selenium in various parts of the plant. Grain (e.g. wheat) can accumulate up to 30 mg/kg without an impairment of growth (Lit. 13).

Waste water containing more than 0.5 mg Se/l is not suitable for irrigation purposes (Lit. 13).

Production and Use/Waste Formation

As a starting material for selenium extraction, the lead chamber sludge that forms during sulphuric acid production can be used or, as often in the USA, the anode sludge from electrolytic purification of copper.

The selenium contained in the lead sludge is first oxidized to selenious acid by heating the sludge together with nitric acid, and then depending on the temperature, this is subsequently reduced with sulphur dioxide to form red or black selenium.

In extracting selenium from the anode sludge produced during the electrolytic purification of copper, the selenite solutions that are to be subsequently reduced with sulphur dioxide are obtained either by roasting with soda and subsequent acid treatment or by heating together with sulphuric acid. The selenium dioxide formed is then passed into water.

The electrical conductivity of the semiconductor selenium depends on the intensity of the incident light. This forms the basis for its use in colourimeters, pyrometers and photoelectric light meters.

Selenium is employed in xerography, rectifiers, for welding purposes, as a magnetic amplifier, as an additive to steel alloys to increase the corrosion resistance, in the rubber industry instead of sulphur for vulcanization and in the glass industry to decolour glass. Selenium compounds play an important role in the paint industry (cadmium sulphoselenide as cadmium yellow and cadmium red) and serve to colour glass, porcelain and artificial resins.

Selenium-containing waste does not occur in large amounts. The major source of such waste is the process for manufacturing and repairing xerox drums. A further source of selenium-containing waste is the sludge from paint production. Selenium is also found in wash water and quenching water, and in the flue dusts from power plants and incinerators (considerable amounts of selenium are contained in newsprint).

Waste Treatment

As the price of selenium is very high, recovery of it by processing selenium-containing waste is, as with aluminium, economical. For example, selenium refineries are equipped with wet scrubbers that employ an approx. 50% solution of hydrobromic acid containing free bromine. The acid fumes are absorbed in a lime and soda bed, and the selenium separated from the hydrobromic acid solution by distillation is recycled.

Otherwise, solid or sludgy selenium-containing wastes from the manufacture or repair of xerox drums or from paint production are disposed of in special dumps.

Literature

1) Woodruff, I.O. and Gies, W.J., Amer. f. Physiol. 6, 29 (1902).

2) Christensen, H.E., Toxic substances; annual list, 1971, Rockville 1971.

3) Cerwenka, E.A. and Cooper, Ch., Arch. Environ. Health 3, 189 (1961).

4) Clinton, M. Jr., J. industr. Hyg. 29, 125 (1947).

5) Sorbe, G., Gefährliche Arbeitsstoffe in Labor und Betrieb, Frankfurt/Main, 1974.

6) Oelschläger, W. and Menke, K.H., Z. f. Ernährungswissenschaft 9, 208 - 222 (1969).

7) le Peintre, C., Contribution à l'édude du selenium et de ses valences dans les eaux naturelles, Diss. Univ. Paris, 1964.

SELENIUM

8) Coulston, F. and Korte, F. (edit.), Environmental Quality and Safety, Vol. II, Stuttgart, New York 1973.

9) Quentin, K.-E., Winkler, H.A. and Weil, L., Schr. Reihe Ver. Wass.-Boden-Lüftung, H. 40, Stuttgart 1973.

10) Hapke, H.-J., Toxikologie für Veterinärmediziner, Stuttgart 1975.

11) Hadjimarkos, D.M. et al, Arch. Environ. Health, 10, 893 - 899 (1965).

12) Ellis, M.M. et al, Proc. Soc. Exp. Biol. and Med. 36 (1937).

13) McKee, J.E. and Wolf, H.E., eds. "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

CADMIUM and CADMIUM Compounds

Cadmium

Formula Cd Cd **CAS no.** 007 440 439

Synonyms

Appearance Silver-white, soft metal

Melting point	312
Boiling point	767
Vapour pressure	
Density	8.64 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	insoluble
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	
Warm-blooded animals	
Fish	
Lower water organisms	

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
		0.2^{++}		5.10^{-5}			I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
	0.006	0.01	0.005	0.005	0.005	

Remarks $^+$ Cd vapour

$^{++}$ Cd vapour and soluble salts

Cadmium oxide

CADMIUM and CADMIUM Compounds

Formula CdO CdO **CAS no.** 001 306 190

Synonyms Cadmium smoke

Appearance Yellow-red to dark brown amorphous powder or lustrous black crystals

Melting point sublimes at approx. 700°C

Boiling point

Vapour pressure

Density 6.95 g/cm^3 (8.15 g/cm^3 cryst.)

Vapour density ratio (air = 1)

Solubility in water

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man 50 mg/m^3 (estimated)+

Warm-blooded animals 72 mg/kg (rats)

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
	0.1	0.1		5.10^{-5}			I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group
	0.006	0.01	0.005	0.005	0.005	

Remarks + inhaled as an aerosol

++ all values relative to Cd

Cadmium and Cadmium Compounds

Description of Material/Use

Cadmium is a silver-white, soft, shiny metal with relatively low melting and boiling points (321°C and 767°C respectively). It is resistant to the action of air, alkalies and sea water.

The figures below show the consumption of cadmium, as a metal or compound, in the following manufacturing processes during 1970 in the Federal Republic of Germany (Lit. 1):

Pigments	Cd_S, CdSe	30%	950	t
Anodes for electroplating		28%	700	t
Battery production	Cd-Ni bat. Cd-Fe bat.	14%	350	t
Salts for electroplating		9%	225	t
Solder alloys		6%	150	t
Electrical lines (Cd-Cu alloy)		3%	75	t
Other alloys and miscellaneous (e.g. nuclear engineering)		2%	50	t
		100%	2,500	t/y

Production (incl. imports) and consumption show an increasing trend.

Cadmium oxide is usually found as an amorphous, yellow-red to dark brown powder. It is insoluble in water and alkalies, highly soluble in dilute acids, ammonium salt and alkali cyanide solutions. Cadmium oxide "smoke" (CdO aerosol) smells sweetly-metallic and is a dangerous source of poisoning.

It is used in electroplating, as a catalyst for organic syntheses, in the manufacture of colours for enamel and sintered materials, in the production of metallic coatings and of selenium ruby glass.

Other cadmium compounds used industrially include:

Compound	Properties	Use
Cadmium acetate $Cd(C_2H_3O_2)_2$	White crystals, highly soluble in water and alcohol	Catalyst in the preparation of vinyl acetate from acetylene and acetic acids; ceramic and porcelain colours
Cadmium cyanide $Cd(CN)_2$	Colourless crystals, highly soluble in water and alkali cyanide	Electroplating
Cadmium chloride $CdCl_2$	Colourless powder, soluble in dilute acids and ammonium salts, insoluble in water and alkalies	Electrodes in Ni-Cd elements; Electroplating
Cadmium nitrate $Cd(NO_3)_2 \cdot 4H_2O$	Colourless, deliquescent crystals, very highly soluble in water	Glass and porcelain colour; Ni-Cd storage batteries
Cadmium carbonate $CdCO_3 \cdot H_2O$	White powder	Starting compound for the production of cadmium pigments, among other cadmium compounds

Compound	Properties	Use
Cadmium stearate $(CH_3(CH_2)_{16}COO)_2Cd$	White, greasy powder, soluble in alcohol and ether, insoluble in water	Light stabilizer for PVC plastics
Cadmium sulphate $CdSO_4$	Colourless crystals, highly soluble in water	Electroplating, starting compound for cadmium pigments, luminescent screens
Cadmium sulphide CdS Cadmium sulphide selenide CdS_xSe_y	Yellow to red powder, soluble in dilute acids, insoluble in water and alkalies	Pigment colours

Hazards to Man

Harmful effects in man may result from

- inhaling cadmium and cadmium oxide dust, CdO "smoke" and dusts of other cadmium compounds (except for cadmium sulphide)
- ingestion of dissolved cadmium compounds.

Occupational accidents are caused primarily by CdO "smoke". As a result of the low boiling point of cadmium, its sublimability and the high oxidizability of the metallic vapour, cadmium oxide "smoke" forms during every thermal treatment of cadmium, e.g.:

- Ore smelting, remelting
- Soldering with aluminium solder or brazing solder
- Welding with cadmium-plated metal parts
- Applying cadmium to metal surfaces (metal spray and metal dip processes)
- Ignition of cadmium dust.

The olfactory threshold is 0.5 ppm.

Short-term exposure to low cadmium concentrations causes attacks of fever ("foundryman's fever") which in favourable cases abate in a few days. Five hours' inhalation of 0.5 - 2.5 mg CdO/m^3 causes pneumonia that lasts for months; 8 - 9 mg CdO/m^3 are fatal for the same duration of exposure (Lit. 2).

The symptoms after acute exposure initially resemble those of a cold and are thus easily mistaken; after a latency period of 10 - 36 hours, inflammation of the respiratory tract, and in serious cases all indications of pulmonary edema, appear.

Chronic illnesses are caused by prolonged uptake of small amounts of cadmium (usually cadmium dust). After a latency period of 2 years, the typical yellow cadmium ring forms on the neck of teeth. The chronic form is characterized by a more or less impaired sense of smell, kidney and lung damage, and possibly painful bone changes (Lit. 3). Protective measures include the wearing of fine-dust masks (IIb) and in the exhausting of the cadmium oxide aerosol.

Illnesses resulting from chronic occupational exposure to cadmium are recognized as occupational diseases (Lit. 4).

Acute poisonings involving dissolved cadmium salts have often been caused by acid-containing food stored in cadmium-plated containers; 30 - 40 mg Cd^{++} (Lit. 3) are supposed to be fatal, but other authors claim only several hundred mg (Lit. 5) are lethal. The initial symptoms are vomiting and diarrhea. Nowadays, the use of cadmium and cadmium alloys for cans used to preserve food, bowls and the like has been restricted or forbidden.

The "Itai-Itai disease" that appeared in Japan between 1939 - 1945 and which is often mentioned in the literature surely involved cadmium ($CdSO_4$; prolonged uptake of approx. 0.6 mg Cd^{++}/day in the drinking water), but it was definitely not the only cause (Lit. 6). Whether zinc can cancel or reduce the toxic effect of cadmium in the human organism is disputed (Lit. 6, 7). Copper is synergistic.

Hazards to the Environment

The cadmium concentration in the soil fluctuates over a wide range. The average value is 0.01 - 0.7 ppm (Lit. 8). In the vicinity of traffic routes (8 m), it increases to 1.8 ppm. A maximum of 14.9 ppm of cadmium was found at a distance of 300 - 600 m from a zinc smeltery (Lit. 1). Superphosphate-containing fertilizers have up to 8 mg Cd/kg. Plants tend to concentrate cadmium in the roots and zinc in the parts above the soil.

Cadmium can also be discharged into the atmosphere wherever large amounts of organic materials are burned. Coal contains 1 - 2 ppm of cadmium, diesel and fuel oil 0.07 - 0.53 ppm, and cigarette smoke 0.016 mg Cd/ 20 cigarettes.

In the Federal Republic of Germany 90 - 180 t of cadmium/ year were discharged into the environment through the burning of coal alone. The zinc-extracting industry is by far the major source. According to Lit. 9, 1247 t of cadmium were emitted by it in 1968 in the USA.

The current act governing the quality of drinking water in the Federal Republic of Germany (1975) allows 0.006 ppm of cadmium/l. In 1971 the Rhine contained up to 2000 mg of cadmium (Lit. 1o). According to Lit. 1, the limit for continued existence of plants and animals in water is 3 - 20 mg/l (cadmium compounds).

The cadmium compounds such as cadmium sulphide and cadmium oxide, which are very slightly soluble in neutral water, dissolve to a noticeable degree in an acidic environment or through the action of moisture, carbon dioxide and sulphur dioxide. As the result of uncontrolled weathering of cadmium sulphide overburden dumps, 0.18 ppm of cadmium were found in a nearby river bed, while mud contained 8 ppm and the mussels living in it 100 ppm (Lit. 1). The latter value clearly shows the accumulating capacity of the organism.

There is no doubt as to the toxicity of cadmium, but there is still great ignorance about the extent and mechanism in the organism.

Production, Waste Formation

Cadmium occurs in nature as greenockite (CdS), otavite ($CdCO_3$) and cadmium oxide (CdO); and further almost always as a companion of zinc, copper and lead ores. The pure minerals have almost no significance technically. Cadmium extraction is thus completely bound to zinc, copper and lead production. As it reduces the rollability of zinc, it automatically occurs here as a byproduct.

The highly volatile cadmium accumulates in the flue dust produced during roasting of the ores. Purification of the electrolytes used for zinc electrolysis and lithopone production likewise provides a cadmium primary product. Cadmium-containing waste, e.g. dead Ni-Cd and Ni-Fe batteries, sprayed metal residues (Cd-Sn alloys) and defective batches from pigment production, are recycled to a large extent.

The raw material is processed either

- by dissolution in sulphuric acid, precipitation of the cadmium with zinc dust (cementation) and subsequent purification (zinc, arsenic, antimony, copper, nickel, iron, manganese, thallium and others) or
- through electrolysis of the cadmium-containing electrolyte formed during the purification of zinc.

A great deal of cadmium-containing waste water is produced in both processes.

Cadmium oxide is obtained using the following methods:

- Vapourization of metallic cadmium and oxidation of the vapour;
- Oxidation of molten cadmium by means of an oxidizing salt;
- Thermal decomposition of cadmium nitrate or carbonate.

Cadmium sulphate is produced by melting cadmium together with ammonium or sodium peroxydisulphate.

Cadmium sulphide is produced in large amounts on a technical scale:

- by direct precipitation from cadmium salt solutions by means of hydrogen sulphide
- by large-scale reaction of cadmium carbonate or oxalate with sulphides
- by calcining cadmium carbonate with sulphur.

The colour depends on the grain size and varies from yellow to orange. Deeper red tones are obtained by means of cadmium sulphide selenide. The sulphide and selenide are precipitated separately or in common and are calcined to obtain a uniform grain size.

See Lit. 11 for the preparation of the above-listed cadmium compounds, which are obtained from very simple chemical reactions.

Waste Treatment

Scrap cadmium and defective batches of cadmium compounds are returned to the production process to a large extent. Organic cadmium compounds or highly contaminated electroplating waste for which processing is not worthwhile in spite of the high cadmium price are brought to special dumps and disposed of there. Incineration of cadmium-containing wastes is virtually out of the question because of the high sublimability of the oxide.

Literature:

1. EEC Commission: Umwelt und Qualität des Lebens. Prepared by: Kienbaum - Unternehmensberatung GmbH, Bummersbach (1973).

2. a) Hoscheck, R,. Gesundheitsgefahren durch Cadmium in "Moderne Unfallgefahren", 18, Vulkan-V. Essen (1974)
   b) Amdur, M.L., Ind. Med. Surg. 22, 251 (1953)
   c) Bonell, I.H., Brit. J. Ind. Med. 12, 385 (1955) Quoted in: Ullmann, Enzyklop. der Technischen Chemiw, Vol. 9, 4th edition Verlag Chemie, Weinheim (1975)

3. Moeschlin, S., Klinik und Therapie der Vergiftungen, G. Thieme-Verlag, Stuttgart (1972)

4. Wagner/Zerlett, Berufskrankheiten der 7. BekV, Kohlhammer-Verlag Köln (1973)

5. Gleason, M.N. et al.: Clinical Toxicology of Commercial Products, Williams, Wilkins, Baltimore (1963)

6. Friberg, L. et al.: Cadmium in the Environment Chemical Rubber C. Press, Cleveland (1971)

7. Shaikh, Z.A. and Lucis, O.J.: Cadmium and Zinc binding in mammalian liver and kidneys Arch. Environm. Health 24, 419 (1972)

8. Yamagata, N. et al.: "Cadmium pollution in perspective", Bull. Inst. Publ. Health 19 (1970), quoted in: Environmental Health Criteria for Cadmium, World Health Organization (1974)

9. OECD: "National Inventory of Sources and Emissions. Cadmium, Nickel and Asbestos, 1968". Report to National Air Pollution Control Administration, Dept. of Health and Welfare, by W.E. Davis and Associates, Leawood, Kansas, USA (1970)

10. Förstner, U., Müller, G.: Schwermetall in Flüssen und Seen, Springer-Verlag Berling (1974)

11. Ullmann - Encyklopädie der technischen Chemie, Vol. 9. 4th edition, Verlag Chemie, Weinheim (1975)

N	ALDEHYDES
N 1	Formaldehyde
N 2	Acrolein
N 3	
N 4	
N 5	
N 6	
N 7	
N 8	
N 9	
N10	
N11	
N12	
N13	
N14	
N15	
N16	
N17	
N18	
N19	
N20	

Formaldehyde (water-free)

FORMALDEHYDE

Formula CH_2O HCHO **CAS no.** 50000

Synonyms Methanal, methyl aldehyde, formic aldehyde, formalin, formol, formyl hydrate .

Appearance Colourless, pungent gas

Melting point	-92°C
Boiling point	-19°C
Vapour pressure	
Density	0.815 g/cm^3 (condensed)
Vapour density ratio (air = 1)	1.03
Solubility in water	very highly soluble
Flash point	<40°C
Ignition temperature	430°C
Inflammable mixture	7 - 73 vol.%

Toxicity range for short-term exposure:

Man	0.5-5 g/kg (10 mg/l chron.)
Warm-blooded animals	100-800 mg/kg
Fish	15-200 mg/l
Lower water organisms	2-100 mg/l

Occupational safety - Danger symbols T + S

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW_1	TA Luft IW_2	TA Luft KL_S	TA Luft KL_G
	6	6	0.07	0.03				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A_1	ENV. 140 (EEC) A_2	ENV. 140 (EEC) A_3	VLWF Group
		0.15				M

Remarks Tear gas 1 mg/m^3 ≙ 0.83 ppm
formaldehyde polymerizes easily 1 ppm ≙ 1.2 mg/m^3

FORMALDEHYDE

Formaldehyde (37-50% solution)

Formula CH_2O **CAS no.**

Synonyms Formalin, formol, formyl hydrate

Appearance Colourless liquid with pungent odour

Melting point	<-15°C
Boiling point	97°C (37% solution)
Vapour pressure	1.3 torr at 20°C (37% solution)
Density	1.11 - 1.13 g/cm^3
Vapour density ratio (air = 1)	approx. 1.03
Solubility in water	very highly soluble
Flash point	50 - 85°C (depending on conc.)
Ignition temperature	430°C
Inflammable mixture	

Toxicity range for short-term exposure:

Man	0.5 - 5 g/kg
Warm-blooded animals	100-800 mg/kg
Fish	15-200 mg/l
Lower water organisms	2-100 mg/l

Occupational safety - Danger symbols T + S

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	6	6	0.07	0.03				I

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^WF Group
			A_1	A_2	A_3	
		0.15				M

Remarks Solution tends to polymerize

Description of Material

Formaldehyde is a colourless, pungent gas that in aqueous solution is present mainly as the hydrate ($HO-CH_2-OH$). It is available commercially under the name "formalin" as a 37% to 50% aqueous solution, stabilized by a methanol content of up to 15% or by addition of benzoguanamine to prevent polymerization to peraformaldehyde. Depending on the intended use, it is employed in the chemical industry also as a 44% unstabilized solution, in the form of various polymers (peraformaldehyde, trioxane, tetraoxane, pentoxane) or in combination with substances that release formaldehyde during synthesis.

Hazards to Man

Formaldehyde forms water-insoluble condensation products (precipitation reaction) with cell protein, thus causing the cells to die. Even very slight amounts such as those formed during the biochemical degradation of methanol block oxidation processes inside the cells and result in overacidification of the aqueous cell content. This substance is thus a strong physiological poison. The olfactory threshold, however, is as low as 0.2 ppm, so that in practice it is possible to guard against health hazards in time.

Inhalation of concentrated formaldehyde vapours causes severe irritation of the mucous membranes and even glottic and pulmonary edema. Ingestion produces corrosive burns in the esophagus and gastrointestinal tract together with sharp pains, vomiting, unconsciousness and collapse.

Retention of urine and perforation of the organs involved may appear as secondary damage. Local eczema and oversensitivity reactions are well-known symptoms to industrial physicians.

The above dangers require special care, such as exhaustion of the vapours formed, protective clothing, safety glasses and respiratory protection, when handling formaldehyde. After an accident the contaminated pieces of clothing should be changed immediately and the areas of skin involved carefully flushed with a great deal of water.

Open flames, sparks and hot surfaces entail the hazard of fire and explosion. Furthermore, there is the danger that lines and vessels containing formaldehyde may become electrostatically charged. Formaldehyde, even when stabilized, must be stored in cool, well-ventilated rooms.

Steel and copper are attacked upon lengthy exposure, so that these metals should not be used for storage containers.

Hazards to the Environment

Because of its poisonous effect on microorganisms, formaldehyde is used as a disinfectant, and its polymerization properties make it useful as a preservative for anatomical and hystological preparations.

Trout that were exposed to a concentration of 10 mg/l of formaldehyde for three days showed no negative changes; with a concentration of 50 mg/l, all trout were dead after the same period (Lit. 1). Using the commercially available 37% solution, the LD_{50} for an American catfish was reached with 25 mg/l (Lit. 1). Algae (Scenedesmus) were adversely affected at concentrations of 0.3 - 0.5 mg/l and Daphnia at a concentration of 2 mg/l (Lit. 2). According to an American investigation, formaldehyde was found to be carcinogenic in rats (Lit. 3).

Production and Use/Waste Formation

Technical production of formaldehyde is accomplished by means of catalytic oxidation of methanol with atmospheric air on silver or copper catalysts (also iron-molybdenum-vanadium catalyst) at 300 - 650°C. This process yields an approximately 40% formaldehyde solution which contains 8 - 10% of methanol (formalin). In addition, direct oxidation of methane with atmospheric oxygen at 450°C and 10 - 20 atmg on an aluminium catalyst is employed. Methanol, acetaldehyde and other oxidation products are formed as byproducts.

Formaldehyde has very many applications in the chemical industry.

As a starting material, formaldehyde is of technical significance in the production of synthetic resins (phenolic and amino plastics, melamine and acetal resins), ethylene glycol, hexamethylene tetramine (Urotropine) and pentaerythrite. The last two compounds are used to make, among others, the highly explosive substances Hexogen, Cyclonite and Nitropenta, and are important as hardeners in artificial-resin chemistry. In addition, formaldehyde is employed in the dye industry for the synthesis of fuchsine, acridine and pyroline dyes, in the mirror industry for silver nitrate reduction, in the rubber industry for the preparation of vulcanizing accelerators, in the textile industry as a protective agent for wool fibres, to increase the stripping power of formaldehyde sulphoxylates, for swell-proof finishing of rayon and rayon staple together with urea, melamine etc, for crease-resistant finishing of textiles, as a tanning agent, for the stabilization of bottoming baths in naphthol dyeing, to improve the water and wash fastness of some direct dyes, in vat dyeing in the form of rongalite, in photo laboratories as a hardener for gelatine films and as an additive to fixing baths, as well as in the synthesis of hydroxymethyl derivatives.

Varying amounts of formaldehyde can occur as waste or waste water in the branches of industry using the above-mentioned manufacturing and processing methods.

This holds especially for plants producing artificial resins, pentaerythrite and ethylene glycol but also for tanneries, textile finishing mills and businesses in which photographic work is done on a large scale.

Waste Treatment

Formaldehyde can be decomposed biologically. To this end, aqueous solutions are fed into sewage treatment plants for secondary treatment (Lit. 4). Residues from distillation and other sludges containing formaldehyde are best disposed of in special waste incinerators.

Literature

1) McKee, J.E. and Wolf, H.E., eds., "Water Quality Criteria", wnd ed., California State Water Resources Control Board, Publication 3-A 1963

2) Bringmann, G. and Kühn, R.
Vergleichende wassertoxikologische Untersuchungen an Bakterien, Algen und Kleinkrebsen.
Gesundh. Ing. 80, 115 - 119 (1959)

3) "Water Quality Criteria Date Book", Vol. 1,
Organic Chemical Pollution of Freshwater
EPA Report No. 18010 DPV 12/70,
A.D. Little, Inc. December 1973

4) Ottinger, R.S., et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", iss. for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973

Acrolein

Formula C_3H_4O CH_2CHCHO **CAS no.** 107028

Synonyms Propenal, acrylaldehyde

Appearance Colourless liquid with pungent odour

Melting point	-87°C
Boiling point	52°C
Vapour pressure	200 torr at 17.5°C
Density	0.84 g/cm³
Vapour density ratio (air = 1)	1.94
Solubility in water	freely soluble (200 g/l at 20°C)
Flash point	-20°C
Ignition temperature	278°C (unstabilized)
Inflammable mixture	2.8 - 31%

Toxicity range for short-term exposure:

Man	5-50 mg/kg
Warm-blooded animals	7-46 mg/kg
Fish	0.05-5 mg/l
Lower water organisms	(4 mg/l) plants

Occupational safety - Danger symbols F + T

Safety guidelines

Air mg/m³	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.25	0.25	0.025	0.01				I

Water mg/l	TWVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.01				

Remarks 1 mg/m³ ≙ 0.4 ppm
1 ppm ≙ 2.5 mg/m³

Description of Material

Acrolein, the simplest unsaturated aldehyde, is a colourless to yellowish, highly volatile liquid. It has a penetrating odour and causes severe tearing. Acrolein is extremely reactive, has a pronounced tendency to polymerize and can thus be stored only in the presence of stabilizers (acetic acid, hydroquinone).

Hazards to Man

Acrolein is a strong irritant. As little as 1 ppm causes heavy tear flow after 2 - 3 min and is unbearable after 5 min. The amount absorbed in this period is very slight and generally is not sufficient to cause toxic symptoms due to resorption. Because of this strong warning sign, concentrations representing a danger to life can be inhaled generally only in the event of accidents.

As a liquid, acrolein causes severe corrosive burns on the skin and mucous membranes. The eyes are particularly endangered (Lit. 1). Ingestion, even of the amount that dissolves in saliva upon contact with an acrolein-containing atmosphere, causes vomiting, a feeling of repletion, and diarrhea. Larger amounts produce circulatory failure (pulmonary edema) relatively rapidly.

For safety reasons, acrolein is processed in closed systems provided with adequate exhaust equipment. Flowing acrolein involves the danger of static charge accumulation. Accordingly, all reactors, lines, distillation columns etc. must be earthed.

Escaping acrolein vapours are heavier than air. They spread out over the floor and can flash back over long distances when ignited (hot surfaces).

Atmospheric oxygen, alkalies, strong mineral acids and peroxides trigger violent polymerization reactions (explosion hazard!).

Hazards to the Environment

Damage to organs, especially liver damage (Lit. 2), was detected in rats after 40 hours' exposure to 2 ppm of acrolein. Ten ppm were fatal after 4 - 6 hours of inhalation, 130 ppm requiring only a short time (Lit. 3).

The toxic concentrations for fish vary within a range of 0.05 - 5 mg/l. Acrolein has been used to kill snails and in the battle against systosomiasis. At a concentration of 3 - 6 mg/l, it is used to kill water plants (Lit. 4).

In an animal experiment (mice), acrolein caused cancer (Lit. 5).

Production and Use/Waste Formation

Acrolein is produced by catalytic oxidation of propylene, acetaldehyde, acrylic acid among others being formed as byproducts. It is an important starting material for the synthesis of amino acids, especially methionine (used to improve feeds), and compounds such as 2-aminopyrimidine, folic acid, quinoline derivatives, glycerine, glutardialdehyde and tetrahydrobenzaldehyde.

Glutardialdehyde is used as a cross-linking agent for proteins and polyhydroxy compounds and as a tanning agent; tetrahydrobenzaldehyde is employed in the production of cycloaliphatic epoxy resins.

Polyhydroxy carboxylic acids synthesized from acrolein, acrylic acid and formaldehyde are superb complexing agents and are important as metal cleaners and baths of liquid rinsing and cleaning agents (Lit. 6).

Acrolein wastes occur both in manufacturing and processing plants. In practice, a separation is not always found, as very often the synthesis of acrolein is coupled with other reaction steps. Nonreusable amounts of acrolein are contained in waste gases and process water from synthesis plants or occur in the form of defective batches and superposed reserves (Lit. 7).

Waste Treatment

Aqueous wastes with low concentrations of acrolein are usually neutralized with sodium hydroxide and fed to a sewage treatment plant for biological secondary treatment.

Concentrated wastes are reprocessed whenever possible or burned in special waste incinerators (Lit. 8).

Literature

1) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", issued for the EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973

2) Murphy, S.D. et al., Toxicolog. Appl. Pharmacol. 2, 183, (1960)

3) Skog, E. Acta Pharmacol. Toxicol. 6, 299 (1950)

4) McKee, J.E. and Wolf, H.E. eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963

5) "Water Quality Criteria Data Book", Vol. 1, Organic Chemical Pollution of Freshwater EPA Report No. 18010 DPV 12/70, A.D. Little, Inc., Dec. 1973

6) Haschke, H. et al., Chem. Ztg. 96, 199 (1972)

7) "Alternatives to the Management of Hazardous Wastes at National Disposal Sites"
Report No. C-74861 to EPA, A.D. Little, Inc. May 1973

8) Patterson, J.W. and Ninea, R.A. "Wastewater Treatment Technology", 2nd ed., published by the Illinois Institute of Technology for Illinois Institute for Environmental Quality, Feb. 1973 (available from NTIS, PB 216162).

O POTENTIALLY UNSTABLE SUBSTANCES O

(excluding fertilizers)

O 1 Styrene
O 2 Dinitrophenol
O 3
O 4
O 5
O 6
O 7
O 8
O 9
O10
O11
O12
O13
O14
O15
O16
O17
O18
O19
O20

Styrene

STYRENE

Formula C_6H_8 C_6H_5 CH CH_2 **CAS no.** 100425

Synonyms Vinyl benzene, ethylene benzene, phenyl ethylene, cinnamol

Appearance Colourless, oily liquid with pungent odour

Melting point	-30.6°C
Boiling point	145°C
Vapour pressure	4.5 torr at 20°C
Density	0.902 g/cm^3
Vapour density ratio (air = 1)	3.6
Solubility in water	very slightly soluble
Flash point	32°C
Ignition temperature	490°C
Inflammable mixture	1.1 - 8%

Toxicity range for short-term exposure:

Man	0.5 - 5 g/kg
Warm-blooded animals	5 g/kg
Fish	25 - 75 mg/l
Lower water organisms	

Occupational safety - Danger symbols Xi

Safety guidelines

Air mg/m^3	**MAK**	**TLV**	**MIK** 1/2 h	24h	**TA Luft** IW_1	IW_2	KL_S	KL_G
	420	420	65	20				II

Water mg/l	**TwVO**	**PLWS**	**ENV. 140 (EEC)** A_1	A_2	A_3	**VLWF Group**
		21				

Remarks 1 mg/m^3 ≙ 0.24 ppm

1 ppm ≙ 4.2 mg/m^3

STYRENE

Description of Material

Styrene is a benzene derivative having a very reactive olefinic side chain. The pure substance is a colourless, oily liquid with a pungent, benzene-like odour. It is inflammable and tends to polymerize. This tendency is so great that the solution already solidifies to a glass-hard mass at room temperature upon exposure to daylight. Technically, this reaction is triggered by adding radical-forming agents. Due to this property, styrene has become an important raw material in the plastics industry.

Hazards to Man

Industrial poisonings involving styrene are caused most often as a result of inhalation of vapours. Liquid styrene can also be absorbed through the skin (resorption rate 9 - 15 mg/cm^2/h (Lit. 1)).

The substance causes strong irritation of the mucous . membranes as well as inflammation of the eyes and upper respiratory tract. Accompanying symptoms are headaches, nausea with vomiting, dizziness, fatigue and general weakness. In serious cases, unconsciousness and cramps, especially stomach cramps, may occur. Nothing is known about harmful effects on organs. On the skin, liquid styrene can cause redness, cracking and inflammation.

Styrene is inflammable. Explosive mixtures which may be ignited by hot surfaces, sparks and open flames form by evaporation. Care must be taken in this regard during processing; electrical equipment must be nonsparking.

For storage, styrene is mixed with inhibitors to inhibit the formation of peroxides, which trigger polymerization. Oxygen, light and strong acids have the same effect. The polymerization can occur explosively. Even in the presence of inhibitors polymerization may take place if the temperature of the solution increases to approx. 50°C. There is the danger of ignition, as these reactions are highly exothermic!

Hazards to the Environment

Investigations have been conducted with mammals and fish. In rats and guinea pigs, inhalation of 1300 ppm (5.5 mg/l) over a period of 139 days caused irritation of the eyes and nose as well as weight loss. The same dose had no effect at all in rabbits and Rhesus monkeys over a period of 264 days (Lit. 2). For rats, the lethal dose (death in coma) was 2500 ppm (10.65 mg/l) for ten hours and 5000 ppm (21.3 mg/l) for 1 hour (Lit. 3).

The lethal dose for oral intake by rats was 5 g/kg (Lit. 2). The LC_{50} after 24 hrs. was given as 57 mg/l for minnows; the toxicity was increased only slightly with a longer exposure (Lit. 4).

Production and Use/Waste Formation

In industry, styrene is produced from ethyl benzene by means of catalytic dehydrogenation over zinc oxide at high temperatures (600°C).

Further methods for producing styrene are: elimination of water from phenyl ethanol, pyrolysis of acetylene, dimerization and dehydrogenation of butadiene.

Styrene is one of the technically most important unsaturated hydrocarbons of the aromatic series. Styrene is used extensively in the plastics industry, because of the ease of polymerization of monomeric styrene to polystyrene. In pure form it serves as an injection moulding compound and insulating material (Trolitul). Together with other reagents, it is used to produce copolymers: with butadiene, the synthetic rubber buna S; with benzoyl peroxide, a firm, clear plastic that, among other things, is suitable for imbedding prepared anatomical specimens. During the processing of uncured synthetic polyester resins, styrene serves simultaneously as a solvent and reactive component. It is used further in the production of emulsifying agents for oils and distillates as well as to interrupt chemical syntheses.

The bulk of styrene waste is produced in petrochemical plants and is found in the condensates of spray towers, old catalysts, and sediments of distillation equipment. Styrene wastes also occur in varying amounts at manufacturers of polystyrene plastics, styrene-butadiene rubber, acrylonitrile butadiene styrene and synthetic styrene acrylonitrile resins (Lit. 5, 6).

Waste Treatment

Water-insoluble components and solids are removed from styrene-containing waste water, which, as a rule, is then fed into sewage treatment plants for biological treatment.

Styrene sludges and solvent mixtures that can no longer be reprocessed are burned in incinerators for special waste (Lit. 7). Cured styrene polymer can also be disposed of together with household refuse.

Literature

1) Dutkiewicz, T., et al.: Skin absorption of toluene, styrene and xylene by man, Brit. J. Industr. Med. 25 (1968) p. 243

2) Wolf, M.A. and coworkers: Toxicological studies of certain alcylated benzenes and benzene. A.M.A. Arch. Industr. Health 14 (1956) p. 387

3) Spencer, H.C. and coworkers
The response of laboratory animals to monomeric styrene.
J. Industr. Hyg. 24 (1942) p. 295

4) Pickering, Q.H. and Henderson, C.
"Acute Toxicity of Some Important Petrochemicals to Fish", J. Water Pollution Control Federation, 38 (9), 1419-29, September 1966

5) Gloyna, E.F., et al.: "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes", Federal Water Pollution Control Administration 1970

6) Condensed Chemical Dictionary
8th ed. New York: van Nostrand Reinhold Company 1971

7) Ottinger, R.S., et al.: "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", iss. for the EPA, TRW Systems Groups, PB 224579, Set/AS, 1 February 1973

2,4-dinitrophenol

DINITROPHENOL

Formula $C_6H_4NO_5$ $C_6H_3(NO_2)_2(OH)$ **CAS no.** 51285

Synonyms d-dinitrophenol, DNP

Appearance Colourless to yellow crystals, explosive when dry

Melting point	sublimes at 114°C
Boiling point	
Vapour pressure	
Density	1.43 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	soluble (6 g/l)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	5-50 mg/kg
Warm-blooded animals	20-200 mg/kg
Fish	5 mg/l no effect
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	0.2	0.2						

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
		0.01				

Remarks Danger of resorption through the skin

Description of Material

Of the six possible isomers, only 2,4-dinitrophenol (DNP) is of technical importance. The colour and shape of the pure, crystalline substance vary depending on the method of crystallization. They are thus no measure of the purity. Usually the crystals are yellow-coloured.

Hazards to Man

2,4-DNP acts on the metabolism as a "decoupler" of respiratory chain phosphorylation. The result is a higher basal metabolic rate with a greatly increasing body temperature. Poisoning is possible by means of resorption through the skin, ingestion and inhalation of DNP dusts or mists when spraying trees and fields. Acute results are at first a sense of well-being, then sweating, restlessness, nausea, fever of up to 40°C, thirst, accelerated breathing, hyperglycemia, collapse and respiratory paralysis. Anginal pain, excess salivation and cramps have also been observed. Acne can occur after local contact. Chronic exposure results in weight loss, damage to the white and red blood corpuscles (blood count), liver and kidney damage, neuritis, impaired vision (cataracts), impaired hearing, yellowing of the skin; 1 g of DNP is lethal.

Special precautionary measures on the job are not required as long as contact with the skin is avoided.

In the laboratory, however, it should be recalled that dry 2,4-DNP reacts violently to impact, friction, heating and ignition (explosion hazard!). For safety reasons, this substance is thus stored moistened with water.

Sublimation takes place upon heating of the crystals. Toxic vapours (ventilation or exhaust equipment are thus necessary) are formed with water vapour.

Hazards to the Environment

In addition to dinitro-ortho-cresol, dinitrophenol is used as an insecticide for the winter spraying of trees and as a weed killer for spraying grain fields. The substance may reach neighbouring surface water in this manner.

The concentrations fatal to fish are between 35 and 200 mg/l. They depend on the hardness of the water (Lit. 1). The oral LD_{50} for rats is 30 mg/kg (Lit. 2).

Production and Use/Waste Formation

Of the known isomers, only 2,4-dinitrophenol is of technical importance. This compound is produced on a large scale by direct reaction of ortho- or para-nitrophenol with concentrated nitric acid. To increase the yield, the starting material is boiled with concentrated sulphuric acid beforehand. Small amounts of 2,6-DNP are formed besides 2,4-DNP. Separation is accomplished by means of fractional precipitation. For this purpose, DNP is converted to the potassium salt and precipitated with barium chloride.

There are numerous other possibilities besides this method, but they are of importance primarily in preparative chemistry (see Beilstein E III 6, p. 654 ff).

Dinitrophenol is an important starting material for azo dyes and sulphur dyes (sulphur black). It is also used to produce explosives, photographic developers, pesticides (chloranil), wood preservatives and to synthesize important compounds such as 2,4-diaminophenol, picric acid, picramide, 2,4-dinitroaniline, metapurpuric acid, among others.

Dinitrophenol reaches the flow of waste primarily via dye manufacturers and, to a lesser degree, explosives manufacturers.

The wastes occurring at manufacturers of DNP are problematical not so much because of their DNP content but rather because of the nitric and sulphuric acids (Lit. 3).

Waste Treatment

Concentrated dinitrophenol wastes should, whenever possible, be returned to the manufacturer for recovery. If such a procedure cannot be handled economically, the wastes are burned. In this case, attention must be given to the emission of nitrogen oxides (special waste incinerators with scrubbers). Wastes with low concentrations are often routed to sewage treatment plants at present and subjected to a secondary, biological treatment. Whether this process suffices to degrade dinitrophenol has not yet been clarified, however (Lit. 3).

Literature

1) McKee, J.E. and Wolf, H.E., eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963.

2) Huguenin, A. et al, Path. et. Biol. 10 (1962) 1707.

3) Ottinger, R.S. et al, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 vols., iss. for the EPA, TRW Systems Group, PB 224579, Set/AS, 1 February 1973.

P MISCELLANEOUS

P 1	Asbestos
P 2	Chlorine
P 3	Phosgene
P 4	Fluorides
P 5	
P 6	
P 7	
P 8	
P 9	
P10	
P11	
P12	
P13	
P14	
P15	
P16	
P17	
P18	
P19	
P20	

Asbestos

ASBESTOS

Formula $Mg_6(OH)_8(Si_4O_{10})$ **CAS no.**

Synonyms Naturally occurring minerals: mountain flax, chrysotile, fibrous serpentine, serpentine asbestos, (crocidolite, hornblende asbestos; blue asbestos)

Appearance Fibrous, interlaced mineral, white or bluish

Melting point	1500°C or (1100°C)
Boiling point	
Vapour pressure	
Density	2.4 - (2.5) g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	virtually insoluble
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man

Warm-blooded animals

Fish

Lower water organisms

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	+)						I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	

Remarks +) preliminary recommended technical values:
fine chrysotile dust 0.15 mg/m^3
fine chrysotile-containing dust 4.0 mg/m^3

ASBESTOS

Description of Material

Asbeston (mountain flax) is a collective name for silicate minerals which, during processing, can be split into flexible fibres of down to microscopic fineness. The fibres are tear-resistant, can be easily spun, heat-resistant, insoluble in water and alkalies and - with the exception of magnesium-rich chrysotiles- also acid-resistant.

Hazards to Man (Lit. 1,2)

Asbestos dusts and asbestos-containing dusts are among the fibrogenic dusts which, with the formation of connective tissue, can simultaneously cause pneumonoconiosis. As a pollutant, asbestos occurs primarily in the form of fine, flexible fibres of 1 - 15 μ in size. Asbestos pneumonoconiosis (asbestosis, mountain flax lung) is an occupational disease that must be reported. The prerequisite for the appearance of this disease is accumulation of fine dust in the alveolar region of the lungs. Fibres of up to 250 μ in length can reach the alveoli. Longer fibres are always more dangerous than short ones.

The first symptoms of disease are irritant coughing, sputum, chest pains and slight shortness of breath. The advanced disease is characterized often by chronic bronchitis, pleural irritation and pleurisy, emphysema and finally severe fibrosis of the lung, which can be fatal. Lung cancer is also often observed in conjunction with asbestosis, occassionally as a delayed consequence.

Sometimes, the action of asbestos can cause irritation of the conjunctiva, gullet and mucous membrane of the larynx. Fine asbestos fibres that reach the digestive tract are occasionally capable of penetrating the stomach and intestinal walls, reaching the blood stream and migrating through the body with the flow of blood. They can even pass through the placenta, so that the fetus may also be endangered (Lit. 3). Members of asbestos workers' families are exposed to such dangers if asbestos dust and fibres are brought home from work via the clothing and hair.

Hazards to the Environment

The environmental hazard of asbestos is limited, because the mineral fibres and dust are quickly deposited by means of precipitation, becoming bound to the soil or sediments, where they are no longer harmful. As with man, only locally high particulate concentrations in the air, feed or drinking water are dangerous for the animal world. Such concentrations can be avoided to a great extent by means of emission reduction measures.

Production and Use/Waste Formation

Asbestos is obtained from naturally occurring mineral reserves of which only a few on the earth are worth mining. None of them are in Germany.

Because of its unique combination of prized properties, asbestos has remained indispensable in numerous areas of application and is used in the manufacture of fire-proof or acid-proof protective clothing, filter cloths for the chemical industry, thermal insulation and heat-resistant electrical insulation, gasket and sealing material, special packagings, asbestos board and paper, asbestos wool as well as various composites with inorganic or organic binders, e.g. asbestos cement ("Eternit"), spray asbestos, magnesia asbestos, It-plates, flooring compounds, break and clutch linings.

Asbestos-containing wastes occur as residues, collected dusts and sludge during processing, use of the products and, under certain circumstances, when tearing down buildings and the like.

Waste Treatment

Asbestos-containing wastes are disposed of by depositing them in dumps. To prevent the formation of dust, the waste should be moistened during loading and unloading and - on dry days - covered immediately after dumping.

Literature

1) Valentin, H. et al.: Arbeitsmedizin, Georg Thieme Verlag, Stuttgart 1971

2) Wagner, R. and Zerlett, G.: Berufskrankheiten der 7. BeKV, Verlag W. Kohlhammer, Stuttgart 1973

3) Cunningham, H.M. and Pontefract, R.D.: Placental transfer of asbestos, Nature 249, 177 - 178, 1974

Chlorine

CHLORINE

Formula Cl_2 **CAS no.** 7782505

Synonyms Chlorine gas, chlorum

Appearance Yellow-green gas, irritating smell

Melting point	-103°C
Boiling point	-34.6°C
Vapour pressure	5048 torr at 20°C
Density	3.214 g/l at 0°C
Vapour density ratio (air = 1)	2.49
Solubility in water	slightly soluble (approx. 2.3 l in 1 l of water at 20°C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	(spec.)
Warm-blooded animals	(100 mg/l, no effect)
Fish	0.05 - 0.6 mg/l
Lower water organisms	0.1 - 25 mg/l

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	1.5	3			0.10	0.30		

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VL^{WF} Group
			A_1	A_2	A_3	
		0.15				

Remarks noninflammable gas 1 ppm ≙ 2.95 mg/m^3

strongly corrosive and toxic gas 1 mg/m^3 ≙ 0.34 ppm

Description of Material

Chlorine is a yellow-green, irritating and suffocating gas 2.5 times heavier than air, so that it collects in a thick layer on the floor when it escapes. As it can be liquefied very easily, it is distributed commercially in (grey-painted) steel cylinders (under a pressure of approx. 6 atm) and tank trucks.

At 20°C and atmospheric pressure, 2.3 litres of chlorine dissolve in one litre of water ("chlorine water"); this is accompanied, after partial dissociation of the chlorine in the water, by the formation of hydrochloric and hypochloric acids.

Chlorine is a very reactive element and reacts with almost all other elements, releasing a great deal of heat. In many of these reactions, however, a certain moisture content in the chlorine is important, e.g. most materials are resistant to chlorine at low temperatures (dry chlorine can be conducted in iron piping, and liquid chlorine stored and transported in steel cylinders), while, except for titanium, moist chlorine attacks almost all technically encountered metals.

Chlorine dissolved in water decomposes upon exposure to sunlight, releasing oxygen. This effect is used in practice for bleaching and disinfecting.

Hazards to Man

Chlorine, especially the moist gas, reacts violently with finely divided metals, producing light. These reactions as well as those of chlorine with volatile organic compounds can occur explosively. Exposure to light is already enough to trigger the reaction. Chlorine detonating gas, a mixture of chlorine and hydrogen that reacts by explosion upon exposure to light or local heating to form hydrogen chloride, is especially dangerous.

Because of the high reactivity of moist chlorine, water should not be used in the event of leakage from a steel container holding chlorine, as the acid then formed will only increase the size of the leak, and the heat released by this reaction will result in more rapid vapourization of the liquid chlorine.

The characterisic, pungent smell of chlorine is already perceived at a concentration of 3.5 ppm chlorine in air. Inhalation of such small amounts may result in "chlorine sniffles"; 15 ppm cause irritation of the throat immediately, while 50 ppm are harmful after only a short exposure. The symptoms of a poisoning are seen immediately in irritation of the eyes, nose and mucous membranes of the respiratory tract; in addition, difficulty in breathing, bloody coughing and a reduced pulse are caused.

Brief inhalation of a concentration of 1000 ppm of chlorine results in such a violent attack on the respiratory organs that death by suffocation occurs within a short period of time as a consequence of the corrosive attack on the respiratory tract and lungs.

Chlorine concentrations of up to 2.0 mg/l do not give pure water any unpleasant taste or smell; if certain organic substances such as phenol are present, however, low chlorine concentrations can cause an undesirable taste or smell in the water. If drinking water must be treated with chlorine because of the possible presence of bacteria, very small amounts of phenol already suffice to give the drinking water an offensive taste, the so-called iodoform or apothecary taste, after chlorination. This can be traced to the formation of chlorophenols. Depending on the sensitivity of the individuals, the critical range yielding a chloryphenol taste is between 0.18 and 0.40 mg/l for chlorine and between 0.002 and 0.170 mg/l for phenol (Lit. 1). Chlorine can impair the taste in tinned and frozen food or result in corrosion of the tins.

Hazards to the Environment

Concentrations of not more than 50 mg/l in irrigation water do not impair the growth of plants; concentrations above this level, however, are harmful to the plants (Lit. 1).

Free chlorine at a concentration of approx. 0.03 mg/l is harmful to fish and other aquatic life (Lit. 1), a distinct temperature dependence being observed. For example, chlorine concentrations of 0.15 to 0.20 mg/l at a water temperature of 4 to 5°C were lethal to carp after an 19-day exposure, while at higher temperatures water with just this chlorine concentration caused no visible harm (Lit. 2).

In the case of lower organisms, concentrations of 0.20 to 0.50 mg/l chlorine cause, as a rule, rapid concentration of protozoa and bacteria, while organisms having a mucilaginous or gelatinous shell are less sensitive; nevertheless, there are types that are extremely chlorine-resistant. The water hog louse, larvae of chironomid and caddis fly as well as certain worms show great resistance (Lit. 3).

Production and Use/Waste Formation

The two major starting materials for the various processes used to produce chlorine are sodium chloride and hydrogen chloride or hydrochloric acid. In the Federal Republic of Germany, the annual production in 1972 was 2932 million t (Lit. 4).

Of the methods starting with sodium chloride, the following are common:

- "Electrolysis of alkali-metal chlorides" in which an aqueous solution of sodium chloride is electrolyzed, using either the diaphragm process or amalgam process. Besides chlorine, hydrogen and sodium hydroxide are products of the electrolysis in both processes; the hydroxide obtained in the amalgam process has a very high purity. After cooling and drying by spraying with concentrated sulphuric acid, the gas is liquefied with the aid of pressure or cold.

- The oxidation of a sodium chloride solution by nitric acid, using the HOPEWELL process at 75 - 125°C and normal pressure.

- In fused salt electrolysis of sodium chloride to obtain sodium in the electrolysis crucible (DOWNS process), chlorine is produced as a byproduct; this is also the case in magnesium extraction, which is performed in a similar manner.

Starting with hydrogen chloride/hydrochloric acid, chlorine can be produced by electrolysis of the hydrochloric acid or chemically by oxidation of the hydrogen chloride. This can be done using manganese dioxide and the WELDON process, which in the meantime has become uninteresting, or directly by means of the DEACON process, which uses air and copper chloride as a catalyst. Improvements of the original DEACON process are the SHELL-DEACON process and a process of the KELLOGG Co.

An interesting method is also so-called oxychlorination, where hydrogen chloride and oxygen are reacted directly with a hydrocarbon.

The industrial applications of chlorine are almost as varied and wide-spread as those of sulphuric acid. Chlorine is needed to produce hydrogen chloride and many chlorides (such as aluminium, iron, phosphorus, cobalt chloride and chloride of lime); it is used to manufacture bleaching solutions, explosives, textile auxiliaries, alkyl chlorides, vinyl and vinyliden chloride as well as pesticides (e.g. DDT and Toxaphen). Chlorine is used in the metallurgical processing of nonferrous metals, to treat water and waste water, in the synthesis of ethylene oxide, in the production of phosgene and as a bleaching agent in the cellulose and paper industries.

The cooling, condensation and spray water obtained upon cooling and liquefying the electrolytically obtained chlorine yield a waste water that is slightly to distinctly alkaline (pH between 7.5 and 9) and contains small amounts of free chlorine (usually less than 5 mg/l; Lit. 5).

In the still currently used process for producing potassium chlorate by feeding chlorine through lime water and subsequent reaction with potassium chloride, waste liquors are produced which sometimes - especially as the result of malfunctions - contain slight amounts of free chlorine.

Although the waste gases occurring during the use of chlorine in organic-chemical production are diverted for reuse, some chlorine does reach the outside air.

Another source of escaping chlorine are the cellulose and paper industries where it is needed for bleaching.

Only very little of the large amounts of chlorine used in manufacturing bleaches and disinfectants as well as in the chlorination of water and waste water escapes into the atmosphere.

Waste Treatment

To prevent hardening and chlorination of the drainage ditch, the waste liquors are concentrated on solid, so-called "fused calcium chloride" (which is also used for freezing mixtures, in the textile industry and in the production of calcium cyanamide) in many chlorine-processing plants. Furthermore, these waste liquors, like the chlorates themselves, are used in weed control.

The chlorine in the vent air of the organic-chemical industry is normally removed by means of scrubbing with water and reused. The efficiency of these scrubbers is quite low; the escaping exhaust air may have chlorine levels of 0.5 to 1.0 volume per cent. Thus, alkaline scrubbing must be employed to achieve lower levels; with efficient scrubbers, the chlorine levels can be reduced to 1 ppm. Otherwise, the exhaust stacks must be sufficiently high.

The waste waters from the alkaline scrubbers contain sodium or calcium hypochlorite and sodium or calcium chloride, depending on whether caustic soda or lime was used. They are also fed to the drainage ditch, after being diluted if necessary.

The valves on old chlorine cylinders (grey steel cylinders) are often already corroded, although the cylinders are not yet empty. Such waste "bombs" are best defused by the fire department or technical emergency service, or returned to the manufacturer. In the latter case transport regulations must be complied with.

Literature

1) McKee, J.E. and Wolf, H.E. eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963

2) Winnacker, K. and Biener, H. Grundzüge der chemischen Technik, Munich, Vienna, 1974, p. 45

3) Ebeling, G. and Schroöder, Th. Zeitschr. f. Fischerei 27 (1929), p. 417 ff

4) Beger, H., Trink- und Brauchwasserbiologie, Stuttgart 1950

5) Meinck, F., Stoof, H. und Kohlschütter, H. Industrie-Abwässer, Stuttgart 1968

Phosgene

PHOSGENE

Formula CCl_2O $CO\ Cl_2$ **CAS no.** 75445

Synonyms Chlorocarbonic acid, carbonyl chloride

Appearance Colourless, almost odourless, noninflammable gas

Melting point	-126°C
Boiling point	8°C
Vapour pressure	1180 torr at 20°C
Density	1.432 g/m^3
Vapour density ratio (air = 1)	3.42
Solubility in water	very slightly soluble, hydrolyzes
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	0.4-40 mg/m^3
Warm-blooded animals	0.4-2000 mg/m^3
Fish	
Lower water organisms	

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	0.4	0.4						I

Water mg/l	TwVO	PIWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
		0.02				

Remarks Tear gas

$1\ mg/m^3 \triangleq 0.24\ ppm$

$1\ ppm \triangleq 4\ mg/m^3$

Description of Material

At room temperature, phosgene is a colourless, almost odourless and noninflammable gas, which can already be liquefied at 8°C and solidifies at -126°C. In the liquid state it is colourless and highly mobile; in solid form it is white and crystalline.

Phosgene is freely soluble in many organic solvents. In water, it decomposes slowly to form CO_2 and H_2O. From a chemical viewpoint, phosgene is the chloride of carbon dioxide and like other acid chlorides is very reactive. It is used in synthesis as a chlorination and dehydrogenation reagent as well as to insert carbonyl and carbonyl chloride groups.

Since phosgene is a dangerous and quickly acting respiratory poison, it was used in World War I as a war gas.

Hazards to Man

Phosgene is one of the most dangerous gases used in industry. Since it does not irritate or give a warning but has merely a barely perceptible smell of mouldy hay, fatal quantities can be inhaled without this being noticed. It is only in the course of hours or days that, after initial queasiness, pulmonary edema develops that can result in death by suffocation or heart failure.

According to the present view of the matter, development of pulmonary edema is causally related to acylation reactions that take place between phosgene and a number of functionally important cell components of the capillaries and epithelium of the lung (Lit. 1). If the poisoned individual survives the pulmonary edema, severe pneumonia may still occur subsequently.

Note: Phosgene can be released, without being noticed, from chlorinated hydrocarbons such as carbon tetrachloride, trichloroethylene and perchloroethylene if these substances come into contact with open flames.

Common subsequent illnesses include embolisms, damage to cardiac muscles, neuritis, encephalitis and metabolic disorders of various kinds (Lit. 2). These effects, however, are reversible. Chronic phosgene poisoning is not known in man.

The safest protection against phosgene poisoning is the use [illegible] fresh-air masks wherever higher phosgene concentrations can be expected.

Hazards to the Environment

It was observed in animal experiments that brief inhalation of 50 - 500 ppm is fatal to most animals. The maximum concentration to which animals can be exposed for a number of hours without being seriously endangered is 0.1 ppm (Lit. 3).

The effect on aquatic life is unknown. After complete hydrolysis, HCl is present as a toxic component.

Production and Use/Waste Formation

Technically, phosgene is produced in a tubular reactor (allowing exact temperature control) by passing carbon monoxide and chlorine over activated charcoal at 40° - 50°C. A gas mixture from which the phosgene is condensed by cooling is formed (Lit. 4). For safety reasons, the bulk of phosgene production is immediately processed further at the manufacturer. Otherwise, it is filled in liquid form into seamless drawn steel cylinders and shipped (Druckgasverordnung/Pressurized Gas Act).

Phosgene has a great variety of applications, in particular chlorination, dehydrogenation and as a carbonyl group source. It is used on a technical scale to produce isocyanates, polycarbonates, metal chlorides, dyes, pharmaceuticals, herbicides, insecticides, carbamic acid chlorides, carbamic acid esters and urea derivatives.

Phosgene waste is found in the waste gases (residual gases) from reaction vessels and containers in which phosgene was produced or processed. Because of its high reactivity, however the amount of phosgene is usually low. Larger amounts are more likely to occur as the result of accidents, ignition of chlorinated hydrocarbons, for instance.

Waste Treatment

Because of the high toxicity, residual gases occurring during production and processing must be purified of phosgene to the greatest extent possible. To this end, they are initially cooled or scrubbed with solvents and then fed to a destruction plant. The type of destruction plant depends on the amount of phosgene to be destroyed.

For small amounts, it suffices to feed the phosgene, together with a parallel stream of water, through a packed tower, where after a sufficient residence time the phosgene is completely hydrolized to HCl and CO_2. The hydrolysis can be accelerated by means of activated charcoal packing.

Larger amounts of phosgene are destroyed using lime water or sodium hydroxide. For catastrophies, plants have been built in which fans draw the phosgene through a tower into which liquid ammonia and steam are simultaneously injected (Lit. 5).

Literature

1) Potts, A.M. and coworkers, The mechanism of action of phosgene and diphosgene. Arch. Biochemistry 24, (1949) p. 329

2) Moerschlin, Sven, Klinik und Therapie der Vergiftung, Thieme Verlag Stuttgart 1972

3) Ottinger, R.S. et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", iss. for EPA, TRW Systems Group, PB 224579, Set/AS 1 February 1973

4) Winnacker, Biener, Grundzüge der chemischen Technik, Carl Hanser Verlag, Munich, Vienna 1974

5) Farbenfabriken Bayer DBP 961681 (1953)

Ammonium bifluoride

FLUORIDES

Formula NH_4HF_2

CAS no. 1341497

Synonyms Ammonium hydrogen difluoride, acidic ammonium fluoride

Appearance Colourless crystals

Melting point 126°C
Boiling point Decomposes at 283°C
Vapour pressure
Density 1.5 g/cm^3
Vapour density ratio (air = 1)
Solubility in water very highly soluble (630 g/l at 20°)

Flash point
Ignition temperature
Inflammable mixture

Toxicity range for short-term exposure:

Man 50 - 500 mg/kg (0.7 - 5 mg/l chron.)
Warm-blooded animals
Fish 2 - 60 mg/l
Lower water organisms 10-200 mg/l bact.

Occupational safety - Danger symbols T + C

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	2.5	2.5					I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
	1.5	0.8-1.7	1.5			L$^+$

Remarks $^+$ as HF

FLUORIDES

Ammonium fluoride

Formula NH_4F

CAS no. 12125018

Synonyms none

Appearance Colourless, flake-like crystals that deliquesce in air

Melting point

Boiling point Sublimation

Vapour pressure

Density 1.32 g/cm^3

Vapour density ratio (air = 1)

Solubility in water very highly soluble (400 g/l at 20°)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man 50 - 500 mg/kg (0.7 - 5 mg/l chron.)

Warm-blooded animals

Fish 2 - 60 mg/l

Lower water organisms 10-200 mg/l bact.

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK 1/2 h	MIK 24h	TA Luft IW$_1$	TA Luft IW$_2$	TA Luft KL$_S$	TA Luft KL$_G$
	2.5	2.5					I	

Water mg/l	TWVO	PLWS	ENV. 140 (EEC) A$_1$	ENV. 140 (EEC) A$_2$	ENV. 140 (EEC) A$_3$	VLWF Group
	1.5	0.8-1.7	1.5			

Remarks

Calcium fluoride

Formula CaF_2

CAS no. 7789755

Synonyms Fluor spar, fluorite

Appearance White powder or colourless crystals

Melting point 1392°C

Boiling point

Vapour pressure

Density 3.18 g/cm^3

Vapour density ratio (air = 1)

Solubility in water virtually insoluble (0.6 mg/l)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man 50 - 500 mg/kg (0.7 - 5 mg/l chron.)

Warm-blooded animals

Fish 2 - 60 mg/l

Lower water organisms 10-200 mg/l bact.

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	**MAK**	**TLV**	**MIK** 1/2 h	**MIK** 24h	**TA Luft** IW$_1$	**TA Luft** IW$_2$	**TA Luft** KL$_S$	**TA Luft** KL$_G$
	2.5	2.5					II	

Water mg/l	**TwVO**	**PLWS**	**ENV. 140 (EEC)** A$_1$	**ENV. 140 (EEC)** A$_2$	**ENV. 140 (EEC)** A$_3$	**VLWF Group**
	1.5	0.8-1.7	1.5			

Remarks

Potassium bifluoride

FLUORIDES

Formula KHF_2

CAS no. 7789299

Synonyms Potassium hydrogen fluoride, hydrofluoride of potassium

Appearance Colourless, hygroscopic crystals

Melting point	approx. 225°C
Boiling point	decomposes above 225°C
Vapour pressure	
Density	2.37 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	very highly soluble (400 g/l at 20°C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg (0.7 - 5 mg/l chron.)
Warm-blooded animals	
Fish	2 - 60 mg/l
Lower water organisms	10-200 mg/l bact.

Occupational safety - Danger symbols

Safety guidelines

Air mg/m^3	**MAK**	**TLV**	**MIK**		**TA Luft**			
			1/2 h	**24h**	**IW$_1$**	**IW$_2$**	**KL$_S$**	**KL$_G$**
	2.5	2.5					I	

Water mg/l	**TwVO**	**PLWS**	**ENV. 140 (EEC)**			**VL^{WF} Group**
			A$_1$	**A$_2$**	**A$_3$**	
	1.5	0.8-1.7	1.5			

Remarks

Potassium fluoride

Formula KF

CAS no. 7789233

Synonyms Fluoride of potassium

Appearance Colourless, hygroscopic crystals

Melting point 846°C

Boiling point 1500°C

Vapour pressure

Density 2.5 g/cm^3

Vapour density ratio (air = 1)

Solubility in water very highly soluble (900 g/l at 20°C)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man 50 - 500 mg/kg (0.7 - 5 mg/l chron.)

Warm-blooded animals

Fish 2 - 60 mg/l

Lower water organisms10-200 mg/l bact

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	2.5	2.5					I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	1.5	0.8-1.7	1.5			

Remarks

FLUORIDES

Sodium bifluoride

Formula $NaHF_2$

CAS no. 1333831

Synonyms Sodium hydrogen bifluoride

Appearance Colourless, crystalline powder

Melting point decomposes above 200°C

Boiling point

Vapour pressure

Density 2.08 g/cm^3

Vapour density ratio (air = 1)

Solubility in water soluble (in hot water)

Flash point

Ignition temperature

Inflammable mixture

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg (0.7-5 mg/l chron.)
Warm-blooded animals	
Fish	2-60 mg/l
Lower water organisms	10-200 mg/l bact.

Occupational safety - Danger symbols T + C

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	2.5	2.5					I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	1.5	0.8-1.7	1.5			

Remarks

Sodium fluoride

Formula NaF

CAS no. 7681494

Synonyms Fluoride of sodium, fluorol (villiaumite)

Appearance Colourless, cubic or tetrahedral crystals

Melting point	992°C
Boiling point	1704°C
Vapour pressure	
Density	2.79 g/cm^3
Vapour density ratio (air = 1)	
Solubility in water	soluble (40 g/l at 20°C)
Flash point	
Ignition temperature	
Inflammable mixture	

Toxicity range for short-term exposure:

Man	50 - 500 mg/kg (0.7 - 5mg/l chron.)
Warm-blooded animals	
Fish	2 - 60 mg/l
Lower water organisms	10-200 mg/l(bact.)

Occupational safety - Danger symbols T

Safety guidelines

Air mg/m^3	MAK	TLV	MIK		TA Luft			
			1/2 h	24h	IW_1	IW_2	KL_S	KL_G
	2.5	2.5					I	

Water mg/l	TwVO	PLWS	ENV. 140 (EEC)			VLWF Group
			A_1	A_2	A_3	
	1.5	0.8-1.7	1.5			

Remarks

Description of Material/Production and Use

Ammonium fluoride: $(NH_4)F$ consists of colourless, flake-like crystals that have a definite ammonia smell and deliquesce in air. The salt is very highly soluble in water and forms a neutral solution. In air or in aqueous solution, a slow transformation to ammonium hydrogen difluoride $(NH_4)HF_2$ and ammonia takes place. If the dry salt is heated, hydrogen fluoride and ammonia form.

To produce $(NH_4)F$, ammonia is fed into an aqueous solution of hydrogen fluoride or $(NH_4)HF_2$ until a saturated solution (warm) of NH_4F is formed, from which the salt crystallizes upon cooling.

Another possibility is to heat a solution of ammonia and NaF, the $(NH_4)F$ formed precipitating as sublimate.

$(NH_4)F$ is used to etch and frost glass, as an additive when printing and dyeing textiles, as an electrolyte additive in the Flussal process (electrolytic process for protecting the surface of magnesium-base metallic materials), as a germicidal agent in the brewing and distilling industries and as a mothproofing agent.

Ammonium bifluoride: $(NH_4)HF_2$ is quite stable, in contrast to the other fluorides of ammonium. It crystallizes in the form of colourless, rhombic prisms, is freely water-soluble and forms a slightly acidic solution.

It is produced by feeding an appropriate amount of ammonia into an aqueous solution of hydrogen fluoride.

Use of $(NH_4)FH_2$ is similar to that of the neutral ammonium fluoride. It is employed to etch glass, disinfect distilling and brewery equipment, as a wood preservative, as a sour bath in laundries, as a rust remover, as an additive in special glasses, in the conversion of silicates, in photography to remove negative films, in the production of decorative protective films on aluminium and aluminium alloys and to pickle metals (electrochemical polishing).

Calcium fluoride: CaF_2 is a colourless, insoluble salt that occurs in nature as the mineral fluorspar.

It is the most important naturally occurring fluorine-containing mineral. It is used primarily in the steel industry as a flux and is also the most important source of fluorine in the chemical industry. In the fabrication of glass, ceramics, enamel, portland cement and abrasive materials, CaF_2 is employed as a flux and opacifier or mineralizer. In addition, it serves as a catalyst in water and hydrogen extraction processes. Calcium fluoride crystals are used to a certain extent as optical filters in IR and UV spectroscopy.

Potassium fluoride: (KF) is a colourless, hygroscopic and freely water-soluble salt. It precipitates from aqueous solution as the dihydrate ($KF \cdot 2H_2O$) and forms cubic crystals that already melt in their own water of crystallization at 41°C. Due to hydrolysis, the aqueous solution of KF is slightly alkaline.

KF is obtained by neutralizing hydrofluoric acid with potash and boiling the solution down, or by calcining the dihydrate.

The technical importance of KF is slight.It is used to fluorate organic compounds in exchange for other halogens, to produce elemental potassium, as a component of fluxes for soldering purposes, as an additive to acid-proof mastics and cement, in the enamel industry, in the production of glazes, to frost glass, as a solvent for barium titanate crystals and as a fire-extinguishing substance for alkali-metal fires, as a disinfecting agent for brewery and distillery equipment and as a component of insecticides.

FLUORIDES

Potassium bifluoride: (KHF_2) is a colourless, hygroscopic and feely water-soluble salt, the solution of which is slightly acidic. It crystallizes in a number of modifications, e.g. as $KF \cdot 2HF$ (mp 72°C) or $KF \cdot 3HF$ (mp 66°C). If the salt is heated (400 - 500°C), potassium fluoride and HF form.

KHF_2 can be obtained from aqueous solutions of potassium hydroxide or potassium carbonate by introducing excess hydrofluoric acid.

It is used, for example, in the production of fluorine, as a flux when soldering silver, as an oxide-dissolving component of powdered aluminium welding fluxes, to etch glass (frosted glass), as a wood impregnating agent, as a disinfecting agent for brewery and distillery equipment, as a rust remover (sour baths in laundries), as a catalyst in polymerization and condensation reactions, to fluorate organic compounds, and to supplement corrosion-preventing fluoride films on Mg and Mg alloys etc.

Sodium fluoride: (NaF) is a colourless, cubic-crystalline salt that is water-soluble and the solution of which is alkaline due to hydrolysis. It occurs in nature as villiaumite. It is produced almost exclusively by neutralization of sodium hydroxide with hydrofluoric acid.

Like the other alkali metals, it is used to preserve wood, in lime glue, paste and adhesives, as a disinfecting agent for brewery and distillery equipment, as a component of insecticides, to a certain extent as medication for tooth treatment and fluorination of drinking water, as a flux in producing open-hearth steel, for soldering and welding of light metals, as an additive to enamel and ceramic materials and also as an optical filter in IR and UV spectrophotometers.

Sodium bifluoride ($NaHF_2$) is a colourless, crystalline salt, the solution of which is slightly acidic. It is produced from sodium hydroxide or sodium chloride and excess hydrofluoric acid and, like potassium hydrogen difluoride, is used as an additive to potassium fluorides in fluorine electrolysis. As a slightly acidic salt, it is used in laundries, as a neutralizing agent for alkalies, to a certain extent, and also as a bleaching agent, since it is capable of dissolving iron oxide.

Hazards to Man (Lit. 5, 6)

The uptake of fluorides can involve either the dissolved fluoride or fluoride sprays and dusts. All soluble fluorides are freely resorbable and highly toxic. The hydrogen salts split off hydrogen fluoride easily, thus providing for additional corrosive attack of the skin and mucous membranes.
The toxic action of these salts is based on the fluoride ions, which are extremely reactive chemically and biologically. They extract the serum calcium from the body by forming insoluble potassium fluoride and react with the cell protein, thus blocking vitally important metabollic processes. (Disturbance of carbohydrate, protein and fat metabolism, inhibition of choline esterase, hyperfunction of the thyroid gland, damage to the musculature).
Because of the many points of the body that are attacked, the symptoms of acute fluoride poisoning are quite general. Besides the symptoms of local action on the gastric and intestinal mucous membranes (vomiting, diarrhea with abdominal pain), fibrillary muscular twitching and general weakness together with epileptiform cramps appear. Even after intake of large amounts of fluoride, death does not occur until after several hours. The causes are circulatory collapse and respiratory paralysis. The acute lethal dose of NaF is 5 - 15 g for man.
The symptoms of chronic poisoning (fluorosis) start slowly and uncharacteristically. It is only after a latency period of more than 6 months that the first typical changes in bone structure, in particular of

the pelvic bones, ribs, vertebrae and teeth, appear. (Osteoporosis, osteomalacia) The consequences are painful joints, swollen joints, enamel defects on the teeth. In addition, there are overall disturbances of the intermediary metabolism that can develop into general cachexia.
When treated in time, the chances of recovery from an acute poisoning are good, considering the circumstances. The treatment of chronic fluorosis is hopeless.

Hazards to the Environment (Lit. 4, 5)

Higher concentrations of fluorides also act in plants and animals as cell poisons, since they block metabolism. There are, however, differences in sensitivity.
In the case of yeasts, it was found that the wild strains are more sensitive to fluorides than the culture yeasts used in brewing. By adding fluorides (1 - 5 mg/l), the undesirable yeasts can be repressed without noteworthy harm to the culture yeasts. In this manner, less fusel oil is formed during alcoholic fermentation.
In gardening, fluoride damage may appear as the result of using wood preservatives (fluorasil), as these substances split off hydrogen fluoride in the wood little by little, which is given off to the environment.
Investigations with soil bacteria (nodule bacteria) as well as germination and growth experiments with domesticated plants indicated that slight amounts of fluoride in the soil may be stimulating. It is only at higher concentrations (above 0.1%) that the toxic action becomes noticeable (Lit. 7). The main danger for plants is not the fluorides dissolved in the soil, but industrially produced fluoride-containing dusts or fluorine gas, since it seems that uptake of fluorides via the roots can be regulated.
The effect of fluorine-containing drinking water on grazing cattle corresponds to that in man. The threshold value at which no harm in cattle raising occurs is about 1 mg/l.

FLUORIDES

The acute lethal doses of NaF are 0.2 - 0.5 g/kg for dogs, 0.1 - 0.5 g/kg for rabbits and 0.25 g/kg for sheep. If cattle feed continually contains more than 40 ppm of fluorine (1.5 mg/kg daily) in its entirety, fluorosis develops in these animals. Sheep are poisoned by 10 ppm of fluoride in feed.

The toxic threshold is 100 ppm for cattle, sheep and pigs; 350 ppm for cocks ; and 500 ppm for hens (Lit. 4). The LD_{50} for trout has been given as 2.3 mg/l (Lit. 8).

Waste Formation

The branches of industry that discharge significant amounts of fluorides into industrial waste water include glassworks, electroplating operations, aluminium and steel makers as well as pesticide and artificial-fertilizer manufacturers. Glass and electroplating waste may contain fluorides in the form of hydrogen fluoride or as the fluoride ion, depending on the pH value of the waste. Silicon tetrafluoride (SiF_4) is a typical fluoride waste from the production of artificial fertilizer from phosphatic rock. The aluminium industry uses cryolite (Na_3AlF_6) as a catalyst for the reduction of bauxite ore. Fluorspar is employed as a flux in steel making, and large amounts of fluorides are absorbed and then released during regeneration of the carbon used as a reducing agent. Nowadays, gaseous fluorides are trapped in gas scrubbers and in the form of aqueous solutions in the waste water flow. The mean fluoride concentrations for aluminium reducing plants are estimated at 107 - 145 mg/l of waste water, and at 1000 - 3000 mg/l for the glass industry (Lit. 9).

Waste Treatment

Industry wastes with a high fluoride concentration are treated in two phases. By adding lime, the soluble fluorides are precipitated as CaF_2 until the concentration has been reduced to 10 mg/l. The compact sludge is disposed of on special waste dumps. The filtrate obtained after precipitation is treated further with alum or activated charcoal until the fluoride concentration is about 1mg/l, after which it is fed into the sewerage system (Lit. 9).

Literature

1) Holleman - Wiberg, Lehrbuch der anorganischen Chemie Berlin 1964
2) Ullman Encyklopädie der technischen Chemie
3) Römpps Chemie Lexikon
4) H.J. Hapke; Toxikologie für Veterinärmediziner Thieme Verlag 1973
5) G. Bredemann; Biochemie und Physiologie des Fluors, Akademie Verlag Berlin 1956
6) H. Valentin a. cowork. ; Arbeitsmedizin Thieme Verlag 1971
7) L. Gisiger; Zur Kenntnis des Fluorions. Seine mikrochemische Bestimmung und seine Wirking auf Pflanzen, Zürich 1931
8) J.E. McKee and H.E. Wolf, eds., "Water Quality Criteria", 2nd ed., California State Water Resources Control Board, Publication 3-A 1963
9) J.W. Patterson and R.A. Minea, "Wastewater Treatment Technology", 2nd ed., issued by the Illinois Institute of Technology for the Illinois Institute for Environmental Quality, February 1973 (available from NTIS, PB 216162).

List of central facilities for the treatment, recycling and disposal of "Other special wastes specific to production" (Item 3.7. of the information document)

Bund-Länder-Ausschuss
Beseitigung von Sonderabfällen
(Federation-Länder Committee on
the Disposal of Special Waste)

August 1974

Type of facility	Location	Operator	Groups of substances
BADEN-WÜRTTEMBERG			
Dump	6909 Malsch, Rhein-Neckar-Kreis	Westdeutsche Deponie GmbH & Co. KG, Duisburg c/o: Haniel Spedition GmbH, 6900 Mannheim E 7, 21 Tel. (0621) 3 89 61	Solid wastes, compact sludges
Detoxication and neutralization	7200 Tuttlingen Im Haslen 2	Tiefbauamt der Stadt Tuttlingen 7200 Tuttlingen Königstr. 2 Tel. (07461) 9 92 61	Solid and liquid cyanogen-containing concentrates, e.g. cyanogen-containing baths, waste from case-hardening shops, but no electroplating sludges; liquid acidic concentrates, e.g. pickling solutions and chrome baths
Detoxication and neutralization	7470 Ebingen, Zollernalb-kreis, Ehestetten 12	Zweckverband der Schmiechagemeinden in 7470 Ebingen Ehestetten 12 Tel. (07431) 27 02	Electroplating sludges, cyanides and chromates in liquid and solid form
Detoxication and neutralization	7220 VS-Schwenningen, Schwarzwald-Baar-kreis, Sewage disposal plant	VS-Schwenningen 7220 VS-Schwenningen Tel. (07720) 6 36 31	a) Chromic acid, acidic and alkaline wastewater b) Cyanogen-containing wastewater c) Oil-containing cyanide wastewater d) Hardening salts
BAVARIA			
Dump	8540 Schwabach Rother Str. 56 Tel. (09122) 85 0 58/59	Zweckverband "Sondermüllplätze Mittelfranken" (SMH) 8510 Fürth Rathaus Tel. (0911) 77 48 02	Pre-treated special waste suitable for dumping

Type of facility	Location	Operator	Groups of substances
B A V A R I A cont'd			
Dump	Gallenbach Lkr. Augsburg-Ost Under construction	Gesellschaft zur Beseitigung von Sondermüll in Bayern mbH. (GSB) 8000 München 23 Herzogstr. 60 Tel. (089) 34 30 39	Pre-treated special waste suitable for dumping
Incinerator	8540 Schwabach Rother Str. 56 Tel. (09122) 85 0 58/59	Zweckverband "Sondermüllplätze Mittelfranken" (SMH) 8510 Fürth Rathaus Tel. (0911) 77 48 02	Organic special waste
Incinerator	8720 Schweinfurt	Gesellschaft zur Beseitigung von Sondermüll in Bayern mbH. (GSB) 8000 München 23 Herzogstr. 60 Tel. (089) 34 30 39	Organic special waste and industrial waste similar to household refuse
Incinerator	8076 Ebenhausen, Lkr. Pfaffenhofen Under construction	GSB (Address above)	Organic special waste
Treatment plant	8540 Schwabach Rother Str. 56 Tel. (09122) 85 0 58/59	SMH (Address above)	Oil-water mixtures including Emulsions Electroplating sludge Acids, bases Hydroxide sludge

Type of facility	Location	Operator	Groups of substances
B A V A R I A cont'd			
Treatment plant	8076 Ebenhausen bei Ingolstadt, Lkr. Pfaffenhofen Under construction	GSB (Address above)	Oil-water mixtures including Emulsions Electroplating sludge Acids, bases Hydroxide sludge
Regeneration of solvents	8192 Geretsried Lkr. Bad-Tölz / Wolfratshausen	GSB (Address above)	Solvents
Collection centre	8000 München-Großlappen (Large-scale collection centre)	GSB (Address above)	See above-mentioned facilities
Collection centre	8900 Augsburg Donauwörtherstr. 310b Tel. (0821) 4 34 40	GSB (Address above)	See above-mentioned facilities
Collection centre	7974 Pfuhl (bei Neu-Ulm) Steinkeule Tel. (0731) 7 18 94	GSB (Address above)	See above-mentioned facilities
Collection centre	8750 Aschaffenburg Staatshafen Tel. (06021) 3 74 96	GSB (Address above)	See above-mentioned facilities

Type of facility	Location	Operator	Groups of substances
B A V A R I A cont'd			
Collection centre	8440 Straubing Hofstetten 100 Tel. (09421) 54 09	GSB (Address above)	See above-mentioned facilities
Collection centre	8359 Sandbach b. Passau	GSB (Address above)	See above-mentioned facilities
B E R L I N			
Dump	1000 Berlin 39 (Wannsee) Rödenbecksteig	Berliner Stadtreinigungs-Betriebe (BSR) 1000 Berlin Ringbahnstr. 96 Tel. (030) 75 02 51	Liquid or sludgy residues free from oil and grease; solid waste
H A M B U R G			
Incinerator	2000 Hamburg 74 Borsigstr. 2	Kommanditgesellschaft AVG Abfall-Verbrennungsgesellschaft mbH. & Co. Tel. (040) 7 33 00 31	Solid combustible waste and separable oil sludges
Incinerator	2000 Hamburg 74 Borsigstr. 2	Baubehörde Hamburg, Stadtreinigung Tel. (040) 2 57 95-1	Solid combustible waste, oil-contaminated active earth, separator sludges and used oils

Type of facility	Location	Operator	Groups of substances
HAMBURG cont'd			
Incinerator	2000 Hamburg 28 Peutestr. 57	Ascalia GmbH., Fabrik chemisch-technischer Produkte Tel. (040) 35 13 66	Used oils, solvents
Detoxication and neutralization	Zentrale Entgiftungsanlage Hamburg 2000 Hamburg 54 Lederstr. 72	Baubehörde Hamburg Amt für Ingenieurwesen III Grundstücksentsorgung 2000 Hamburg 1 Hammerbrockstr. 95 Tel. (040) 2 48 25	Acidic, alkaline, cyanide and chromate concentrates, in addition to developing and fixing baths
Acid sludge cracking plant	2000 Hamburg 28 Hovestr. 50	Norddeutsche Affinerie 2000 Hamburg 36 Alsterstr. 2 Tel. (040) 4 41 96-1	Acid sludges and waste acids from the mineral oil industry
HESSE			
Underground dump	6431 Herfa-Neurode Lkr. Hersfeld	Kali und Salz AG Hauptverwaltung 3500 Kassel 1 Postfach 407 Tel. (0561) 30 11	Distillation and hardening salt residues that do not release gas or increase in volume
Dump	6251 Offheim, Kr. Limburg	Westdeutsche Deponie GmbH. & Co. KG 6200 Wiesbaden Adelheidstr. 23 Tel. (06121) 37 04 05	Industrial waste including compact sludges

Type of facility	Location	Operator	Groups of substances
HESSE cont'd			
Incinerator	6081 Biebesheim, Kr. Groß-Gerau	Südhessische Verbrennungs GmbH. 6081 Biebesheim Industriegebiet Tel. (06258) 60 61	Oil-water mixtures; Emulsions from the metal working industry Oil sludges; Solid matter, e.g. used tyres
LOWER SAXONY			
Dump	3201 Hoheneggelsen, Lkr. Hildesheim - Marienburg	Verbrennungsgesellschaft für Industrieabfälle GmbH. & Co. KG (Vfl) 3201 Hoheneggelsen Ziegeleiweg Tel. (05129) 313 u. 466	Solid matter; Pasty substances, e.g. Arsenic-containing refuse; Paint residues; Oil-contaminated earth; Electroplating sludge
Incinerator	4550 Bramsche, Lkr. Osnabrück	Gewässerschutz GmbH. 4550 Bramsche 3 Achmer, Am Kanal Tel. (05461) 34 21	Combustible liquids, e.g. Used oil; Solvents; Emulsions
NORTH RHINE-WESTPHALIA			
Dump	4035 Breitscheid, Kr. Düsseldorf - Mettmann	Elisabeth Muscheid 4035 Breitscheid Haus Muscheid Tel. (02102) 2 16 81	Filter residues from organic production; Waste from production of detergents; Residues from production of adhesives; Distillation residues from production of glycerin; Inorganic production residues; Boiler house granulates

Type of facility	Location	Operator	Groups of substances
NORTH RHINE-WESTPHALIA cont'd			
Dump	4650 Gelsenkirchen Widehopfstr. 30 Tel. (02322) 7 25 64	Zentraldeponie Enscherbruch GmbH 4300 Essen Kettwiger Tor Tel. (02141) 23 93 57-59	Solid wastes and compact sludges
Dump	4035 Breitscheid, Kr. Düsseldorf - Mettmann	Westdeutsche Abfallbeseitigungsgesellschaft mbH. & Co. KG (WESTAB) 4100 Duisburg Hafenstr. 4 Tel. (02131) 80 61	Oil-contaminated earth, Filter earth from sewage treatment; Residues from oil tank cleaning; Slag from aluminium processing; Plastic waste; Grinding and electroplating sludges; Miscellaneous
Dump	5628 Heiligenhaus, Kr. Düsseldorf - Mettmann	Kreis Düsseldorf-Mettmann Tel. (02104) 79 02 52 In cooperation with Ruhrverband 4300 Essen Tel. (02126) 30 10	Hydroxide sludges from electroplating, pickling and anodizing shops
Detoxication, neutralization and dewatering plant	5860 Iserlohn Kläranlage Iserlohnerheide	Ruhrverband 4300 Essen Kronprinzenstr. 37 Tel. (02141) 22 10 13 By order of the Gesellschaft für Wirtschaftsförderung Iserlohnerheide mbH.	Electroplating concentrates and semi-concentrates, Wastewater from pickling shops, Metal hydroxide sludges

Type of facility	Location	Operator	Groups of substances
NORTH RHINE-WESTPHALIA cont'd			
Sludge dewatering plant	5628 Heiligenhaus, Kr. Düsseldorf - Mettmann	Ruhrverband (Address above) By order of the Oberkreisdirektor Düsseldorf - Mettmann 4020 Mettmann Düsseldorferstr. 26 Tel. (02104) 21 61	Hydroxide sludges
Detoxication, neutralization and dewatering plant	4800 Bielefeld Zentrale Entgiftungsanlage Bielefeld	Stadt Bielefeld - Tiefbauamt - 4800 Bielefeld Viktoriastr. 7	Electroplating concentrates with chromate cyanide and nitrile; Acids and alkalies; Hydroxide sludges
Emulsion treatment plant	4630 Bochum-Riemke Projected	Gelsenberg-Mannesmann-Umweltschutz-GmbH 4300 Essen 1 Postfach 3 Tel. (02141) 72 21	Used oils; Solvents; Emulsions
RHINELAND PALATINATE			
Dump	6711 Gerolsheim, Lkr. Bad Dürkheim	Fa. Südmüll 6711 Frankenthal Mörscher Weg	Household and bulky refuse; Industrial refuse in drums; Compact sludge and cover material

Type of facility	Location	Operator	Groups of substances
RHINELAND PALATINATE cont'd			
Detoxication, neutralization and dewatering plant	6680 Neunkirchen - formerly Grube König - Projected	Südwestdeutsche Fernwärme GmbH 6600 Saarbrücken Sulzbachstr. 26 Tel. (0681) 3 95 60	Acids, alkalies; Non-compact neutralization sludges; Electroplating sludges; Waste from pickling and case-hardening shops, burnishing plants etc.
Incinerator	6601 Camphausen - Gelände der Grube Camphausen - Projected	Südwestdeutsche Fernwärme GmbH (Address above)	Waste from industrial and commercial pla Hospital waste; Used oils; Spent solvents; Emulsions; Compact sewage sludges; Oil and paint sludges; Residues from benzine extractors (petrol traps) and oil separators
SCHLESWIG-HOLSTEIN			
Incinerator	Kiel - Hassee	Müllverwertung Nord GmbH & Co. KG 2300 Kiel Rendsburger Landstr. 246 Tel. (0431) 68 28 95	Used oil and other oil-containing wastes
Used oil dewatering plant	Flensburg Klärwerk Kielseng	Stadt Flensburg u. Lkr. Flensburg Rathaus Tel. (0461) 8 54 25	Oil-water mixtures

Type of facility	Location	Operator	Groups of substances
SCHLESWIG-HOLSTEIN cont'd			
Ship de-oiling plant (bilge de-oiling)	Lübeck Teerhofinsel	Bitunamel Feldmann & Co. KG Teerhofinsel Tel. (0451) 2 21 12	Oil-water mixtures
Regeneration of solvents	Tornesch	Brennerei und Chemische Werke 2082 Tornesch Tel. (04122) 53 24 (Ütersen)	Solvents excepting chlorinated hydrocarbons
Regeneration of solvents	Trittau	System-Chemie Trittau Rudolf Schmitohloff KG 2077 Trittau Bunsenstr. 3 Tel. (04154) 20 86	Chlorinated hydrocarbons: Trichloroethylene Perchloroethylene Methyl chloride Trichloroethane
Emulsion treatment	Kiel Hassee	Müllverwertung Nord GmbH & Co. KG 2300 Kiel Rendsburger Landstr. 246 Tel. (0431) 68 28 95	Emulsions
Ship de-oiling plant (bilge de-oiling)	Kiel Wik Scheerhafen	Harry Stallzus Kiel Wik Scheerhafen Tel. (0431) 3 09 01	Oil-water mixtures

Type of facility	Location	Operator	Groups of substances
OTHER FACILITIES			
Incinerator ship M/T "Mathias I" M/T "Mathias II"	General agent: Südmüll GmbH & Co. 6710 Frankenthal/Pfalz Postfach 510 Tel. (06233) 75 53	SSB Stahl- u. Blechbau GmbH 4630 Bochum-Lancandneer Warnburgstr. 13 Tel. (02321) 28 72 19 Telex: 08/25 519	Incineration of pumpable liquid mixtures of substances (hydrocarbons) at sea
Incinerator ship M/T "Vulcanos"	General agent: Westab GmbH & Co. KG 4100 Duisburg-Ruhrort Hafenstr. 4 Postfach 130 420 Tel. (02131) 80 61 Telex: 08-55 321	OCS Ocean Combustion Service BV Rotterdam-3020 14 Doodewaardstraat P.O. Box 608 Tel. 010-67 15 36 (commercial) 010-29 17 95 (technical) Telex: 21 512	Incineration of pumpable liquid mixtures of substances (hydrocarbons) at sea

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Explanations of Terms

Additional purification stage

In this connection, this refers to a secondary treatment stage which further lowers the concentration of a substance in a flow of waste that has already passed through a primary treatment stage.

Adsorption

The adherence of a substance to the surface of another solid or liquid substance.

Aerated

Mechanical introduction of air for the chemical and biochemical decomposition of waste or waste water through the action of oxygen.

Aerobic

Requiring air, especially atmospheric oxygen.

Alkyl

Refers to organic compounds the carbon atoms of which are connected by straight or branched chains and not by rings (opposite: aryl or cyclic).

Alveoli

Sac of a gland or air sac of the lung.

Amphoteric, amphoterism

Characteristic of compounds that, depending on the conditions encountered, are acidic or basic.

Anaerobic

In the absence of oxygen.

Anhydrides

Compounds that are obtained by extracting water (chemical action, heat) from organic or inorganic acids.

Anion

Negatively charged ion.

Aryl

Refers to organic compounds containing one or more atomic rings.

Carcinogenic

Having the capacity to cause or form cancer.

CAS Registration Number

A number assigned by the Chemical Abstracts Service to unambiguously identify a chemical substance.

Catalysis

Augmentation of the rate of a chemical reaction by a substance (catalyst) which itself is not consumed.

Cation

Positively charged ion.

Cementation

Consolidation of waste by the injection of cement or by chemical reaction with substances causing consolidation.

Chemical

A word with a wide meaning including the element, compounds and mixtures (refer also to these words).

Coagulation

Flocculation of particles to collect impurities; initiated by chemicals.

Collapse

Shock and its phases.

Coma

Extremely deep state of unconsciousness.

Compact

Sludges with a water content ≤ 70 %

Compound

Molecule built up from the same or different types of atoms.

Concentration

The relative fraction of one substance in another, normally expressed in weight percent, volume percent or as weight/volume.

Degradation, decomposition

Chemical or biological transformation of a complex compound into a number of simple ones.

Deliquescence, deliquescent

The ability to absorb water from the air.

Dermatitis

Inflammation of the skin.

Dermatoses

Skin diseases.

Diuretic

Any agent that increases the volume and flow of urine.

Element

A pure basic substance consisting of atoms; cannot be broken down further by chemical means.

Emissions

The air pollutants, noises, vibrations, light, heat, radiation and the like generated by a plant.

Emphysema

Distension of tissue. Here, overdistension of the air spaces in the lungs.

Eutectic

Designation for a certain mixture of two or more substances that form a homogenous melt or solution but which are immiscible in the solid state.

Flow of waste

All waste occurring in a certain process. Often denotes a liquid discharge, but is also applied to gaseous emissions or solid waste.

Fibrosis, fibrogenic

Growth of connective tissue in excess of that naturally present.

Fungicide, fungicidal

Designation for chemicals that kill or inhibit the growth of fungi and their spores.

Gangrene

Death of tissue due to failure of blood supply to an area.

Heavy metal

Metallic elements having a high density (> 5 g/cm^3); toxic for the most part.

Haemolysis

Destruction of red corpuscles with the release of haemoglobin.

Hydrolysis

Dissociation of a chemical compound by water.

Hygroscopic

See "Deliquescence"; property observed usually in very highly water-soluble salts.

Immissions

Air pollutants, noises, vibrations, light, heat, radiation and so on acting on humans, animals, plants or other objects.

Incineration

Controlled burning of waste during which primarily gaseous emissions are produced.

Inorganic

Describes chemical compounds without carbon atoms (some extremely simple carbon compounds are also designated inorganic).

Ion

The electrically charged part of a molecule.

Mixture

A combination of two or more compounds; actually, all untreated waste consists of mixtures.

Molecule

A combination of two or more atoms held together by chemical bonds.

Mutagenic

The ability to cause a permanent, hereditary change, different from that of the parents, in the nature of a descendant.

Necroses, necrotic

Death of tissue, dead, gangreneous.

Neurasthenia

A physical state characterized by fatigue, headaches, unusual sensitivity etc.

Neutralization

Adjustment of the pH to a value of 7 by means of acids or bases.

Oral

Intake via the mouth.

Organic

Refers to chemical compounds containing carbon atoms.

Paresthesia

Tingling, crawling or burning sensation of the skin.

pH

Measure of the acidity or basicity of a chemical solution (value of 0 to 14); a pH of 7 indicates a neutral solution, smaller numbers indicate increasing acidity and larger numbers increasing basicity.

Pneumonia

Inflammation of the lungs.

Polymerization

Mode of origin of high-molecular compounds.

Pond (lagoon)

Shallow, usually artificial pond in which waste water is left to undergo natural processes.

ppb

Parts per billion. $(1 : 10^9)$

ppm

Parts per million. $(1 : 10^6)$

Salt

The compound of the anion from an acid and a metal cation.

Scrubbing

Removal of impurities from a gas stream by spraying of a liquid.

Sedimentation

Settling of solids under the action of gravity.

Sensitization

Making the body or certain tissues sensitive to foreign substances, so that repeated contact with the sensitizing substance at a later date causes oversensitivity reactions.

Special (waste) dump

A special dump in which wastes that cannot be disposed of together with household refuse can be disposed of in a proper manner. Such dumps are, as a rule, sealed against the penetration of ground water, and perhaps surface and rain water, and have collecting and treatment basins as well as a drainage system for seepage.

Special waste incinerators

A special incinerator for solid, liquid and sludgy waste that cannot be disposed of together with household refuse nor in special dumps. Such incinerators have suitable equipment for flue gas treatment, since, as a rule, high concentrations of harmful gas are formed during combustion.

Special waste treatment plant (facility)

A plant (facility) in which waste that cannot be disposed of together with household refuse is subjected to a special treatment or pretreatment, e.g. neutralization, detoxication, dewatering, emulsion separation, distillation etc.

Synergism

Cooperative action where the total effect of individual substances is greater than the sum of the individual effects of the substances.

Teratogenic

The ability to cause malformations. (not in the hereditary endowment).

Uraemia

Poisoning of the body by toxic substances retained in the blood due to incapacity of the kidney to filter and excrete them in urine.

Waste balance

The sum total of substances representing the difference between raw material input and product output.

VI . Literature

A list of literature used for the substance in question is to be found at the end of each data sheet. In addition, the following more detailed and extensive literature was used when preparing this manual:

1) Capener, E., Wright, R. M., Brown, S. L., Stanford Research Institute Menlo Park, California: Draft Manual of Hazardous Waste, prepared on behalf of the Federal Ministry of the Interior, Bonn, April 1974

2) R. S. Ottinger et al., "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", 16 volumes, issued for EPA, TRW Systems Group, PB 224579, Set/AS, 1.2.1973

3) Informationsschrift "Sonderabfälle", compiled by the Bund-Länder-Ausschuß "Beseitigung von Sonderabfällen" (Federation-Länder Committee on the "Disposal of Special Waste"). Edited by Länderarbeitsgemeinschaft Abfallbeseitigung in cooperation with the Federal Minister of the Interior in February 1975

4) G. Hommel, Handbuch der gefährlichen Güter, Springer Verlag, Berlin, 1973/74

5) Graf, W., Eulenberg, P., Webner, D., Merkblätter gefährlicher Stoffe, Verlag W. Kohlhammer, Berlin 1974

6) Schmidt, L., Gerfährliche Stoffe, loose-leaf collection, Deutscher Fachschriftenverlag Braun & Co. KG, Mainz-Wiesbaden, February 1975

7) Kumpf, W., Maas, K., Straub, H., Müll- und Abfallbeseitigung (Müllhandbuch), Erich Schmidt-Verlag, as per 1975

8) Römpp, M., Chemielexikon, Franck'sche Verlagshandlung Stuttgart, 6th and 7th editions

9) Hollemann, A. F., Wiberg, E., Lehrbuch der anorganischen Chemie, Walter de Gruyter Verlag, Berlin 1971, 71st - 80th editions

10) Gmelin, Handbuch der anorg. Chemie, Springer Verlag, Berlin

11) D'Ans, Lax, Taschenbuch der Chemiker und Physiker, 3rd edition, Springer Verlag Berlin, 1967

12) Handbook of Chemistry and Physics, edited by Weast, R.C., CRC-Press, Cleveland 1973-74, 54th edition

13) Keune, M., Augustin, M., Demus, D., Taeger, E., Chimica - ein Wissensspeicher, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1972, Volumes I and II

14) Ullmanns Encyklopädie der techn. Chemie, Verlag Chemie, Weinheim/Bergstraße, 3rd and 4th editions

15) Henglein, F. A., Grundriss der chemischen Technik Verlag Chemie Weinheim 1968

16) W. Leithe; Die Analyse der Luft und ihrer Verunreinigungen, Wissenschaftl. Verlagsanstalt, Stuttg., 1974

17) Althaus, H., Jung, K.-D.; Wirkungskonzentration gesundheitsschädigender bzw. toxischer Stoffe in Wasser für niedere Wasserorganismen sowie kalt- und warmblütige Wirbeltiere einschließlich des Menschen bei oraler Aufnahme des Wasser oder Kontakt mit dem Wasser. Kurzfassung einer Literatur- und Datendokumentation.
Hygiene-Institut des Ruhrgebiets, Gelsenkirchen, 1973

18) Wirth, W., Hecht, G., Gloxhuber, C.,
Toxikologie-Fibel
Georg-Thieme Verlag, Stuttgart 1971, 2nd edition

19) Moeschlin, S., Klinik und Therapie der Vergiftungen, Georg-Thieme Verlag, Stuttgart 1972, 5th edition

20) Winnacker-Biener, Grundzüge der chemischen Technik, Carl Hanser Verlag, Munich-Vienna, 1974

21) Valentin, M. et.al., Arbeitsmedizin, Georg-Thieme Verlag Stuttgart 1971

22) Sorbe, G., Gefährliche Arbeitsstoffe in Labor und Betrieb, Umschau-Verlag, Frankfurt/Main 1974, 2nd edition

23) Flury, F.. Zernik, F., Schädliche Gase, Springer Verlag, Berlin 1969

24) Wagner, Zerlett, Berufskrankheiten der 7. BeKV Verlag W. Kohlhammer Berlin, 2nd edition, 1973

25) Braun, W., Dönhardt, A., Vergiftungsregister Georg-Thieme Verlag, Stuttgart 1970

26) Fodor, G., Schädliche Dämpfe, VDI-Verlag Düsseldorf 1972

27) Tutsch, D., Taschenlexikon der Medizin, Verlag Urban und Schwarzenberg, Munich, Berlin, Vienna 1975

28) Hapke, H. J., Toxikologie für Veterinärmediziner Ferdinand Enke Verlag, Stuttgart, 1975

VII/1. MAJOR GROUP INDEX

The letters identify the individual groups of substances, the numbers individual substances within a group. This index is for classification purposes only; it is not meant to be used to locate individual compounds (see VII/2.= Alphabetical Index).

A	Organohalogen compounds
A 1	Epichlorohydrin
A 2	Trichloroethane
A 3	Dichloroethane
A 4	Dibromoethane
A 5	Ethylene Chlorohydrin
A 6	Allyl Chloride
A 7	Methyl Chloride
A 8	Carbon Tetrachloride
A 9	Chloroprene
A10	Dichlorodiisopropyl Ether
A11	1,2-Dichloropropane

B	Organic sulphur, nitrogen, nitro and phosphorus compounds, excluding biocides
B 1	Aniline
B 2	Nitrotoluene
B 3	Nitrobenzene
B 4	p-Chloronitrobenzene

C	Isocyanates
C 1	Toluene Diisocyanate
B 2	Diphenylmethane-4,4-diisocyanate

D	Nitriles
D 1	Acrylonitrile

E	Cyanides and substances which can form cyanides
E 1	Hydrogen Cyanide
E 2	Sodium Cyanide
E 3	Potassium Cyanide
E 4	Calcium Cyanide

F	Polycyclic hydrocarbons, including condensed systems

G	Phenols and their derivatives
G 1	Phenol
G 2	Cresol
G 3	Benzoquinone
G 4	Pentachlorophenol

H	Solvents without organohalogen compounds
H 1	Xylol
H 2	Benzene
H 3	Toluene

I	Biocides, pharmaceuticals and compounds derived from them, including pesticides

K	Tars and tar-like products
K 1	Carbolic oil
K 2	Carbolineum

L	Organic and inorganic acids, bases and anhydrides
L 1	Maleic Anhydride
L 2	Hydrogen Fluoride
L 3	Hydrogen Chloride
L 4	Potassium Hydroxide
L 5	Sodium Hydroxide
L 6	Nitric Acid
L 7	Sulphuric Acid
L 8	Fluosilicic Acid
L 9	Acetic Anhydride
L10	Oxalic Acid
L11	Phthalic Anhydride
L12	Benzenesulphonic Acid

M	Metals, metallic compounds or metal-containing inorganic or organic compounds of the following metals
M 1	Mercury
M 2	Lead
M 3	Arsenic
M 4	Beryllium
M 5	Antimony
M 6	Chromium
M 7	Selenium
M 8	Cadmium

N Aldehydes

N 1 Formaldehyde
N 2 Acrolein

O Potentially unstable substances (explosive, strongly oxidizing, polymerizing etc.)

O 1 Styrene
O 2 Dinitrophenol

P Miscellaneous

P 1 Asbestos
P 2 Chlorine
P 3 Phosgene
P 4 Fluorides

VII/2. ALPHABETICAL INDEX

The underlined names are the names at the top of the cover sheet for a data sheet. The names that are not underlined are the synonyms listed in the data sheet.

A

Acetate of lead M 2
Acetio anhydride L 9
Acidic ammonium fluoride P 4
Acrolein N 2
Acrylaldehyde N 2
Acrylonitrile D 1
Allyl chloride A 6
Aminobenzene B 1
Aminophen B 1
Ammonium bifluoride P 4
Ammonium fluoride P 4
Ammonium hydrogen difluoride P 4
Anglesite M 2
Anhydrous hydrochloric acid L 3
Anhydrous hydrofluoric acid L 2
Aniline B 1
Aniline oil B 1
Antimony M 5
Antimony bloom M 5
Antimony hydride M 5
Antimony (III) oxide M 5
Antimony trioxide M 5
Aqua fortis L 6
Arsenate of calcium M 3
Arsenic hydride M 3
Arsenic (III) oxide M 3
Arsenic trioxide M 3
Arsenous oxide M 3
Arsine M 3
Asbestos P 1

B

Basic chromium (III) sulphate	M 6
Benzene	H 2
Benzenesulphonic acid	L12
Benzol	H 2
Benzoquinone	G 3
Beryllia	M 4
Beryllium	M 4
Beryllium chloride	M 4
Beryllium fluoride	M 4
Beryllium hydroxide	M 4
Beryllium oxide	M 4
Blue asbestos	P 1

C

Cadmium	M 8
Cadmium acetate	M 8
Cadmium carbonate	M 8
Cadmium cyanide	M 8
Cadmium chloride	M 8
Cadmium nitrate	M 8
Cadmium oxide	M 8
Cadmium smoke	M 8
Cadmium stearate	M 8
Cadmium sulphate	M 8
Cadmium sulphide	M 8
Cadmium sulphide selenide	M 8
Calcium arsenate	M 3
Calcium cyanide	E 4
Calcium fluoride	P 4
Carbolic acid	G 1
Carbolic oil	K 1
Carbolineum	K 2
Carbon tetrachloride	A 8
Carbonyl chloride	P 3
Caustic potash	L 4
Caustic soda	L 5

Ceruse	M 2
Cerussite	M 2
Chlorine	P 2
Chlorine gas	P 2
Chlorobutadiene	A 9
2-Chlorobutadiene-(1,3)	A 9
Chlorocarbonic acid	P 3
1-Chloro-2,3-epoxypropane	A 1
2-Chloroethanol	A 5
2-Chloroethyl alcohol	A 5
Chloromethane	A 7
Chloromethyloxirane	A 1
Chloronitrobenzene	B 4
p-Chloronitrobenzene	B 4
Chloroprene	A 9
3-Chloroprene	A 6
3-Chloropropylene	A 6
1-Chloropropylene oxide	A 1
Chlorothene	A 2
Chlorum	P 2
Chromate of potassium	M 6
Chromate of zinc	M 6
Chrome yellow	M 6
Chromic anhydride	M 6
Chromium (III) hydroxide	M 6
Chromium (VI) oxide	M 6
Chromium trioxide	M 6
Chrysotile	P 1
Cinnamol	O 1
Cologne yellow	M 6
Corrosive sublimate	M 1
Cotunnite	M 2
Cresol	G 2
Cresylic acid	G 2
Crocidolite	P 1
Cyanogran	E 2

D

Desmodur 44	C 2
Desmodur T 65, T 80	C 1
Dibromoethane	A 4
1,2-Dibromoethane	A 4
Dichlorodiisopropyl ether	A10
Dichloroethane	A 3
1,2-Dichloroethane	A 3
2,2-Dichloroisopropyl ether	A10
Di-(2-chloro-1 methyl-ethyl) ether	A10
1,2-Dichloropropane	A11
Dichromate of potassium	M 6
4,4'-Diisocyanato-diphenylmethane	C 2
Dimethylbenzene	H 1
2,4-Dinitrophenol	O 2
d-Dinitrophenol	O 2
2,5-Dioxo-dihydrofuran	L 1
1,3-Dioxo-phthalan	L11
p,p'-Diphenylmethanediisocyanate	C 2
Diphenylmethane-4,4-diisocyanate	C 2
DNP	O 2

E

Epichlorohydrin	A 1
1-Epichlorohydrin	A 1
Essence of mirbane	B 3
Ethanoic anhydride	L 9
Ethylene benzene	O 1
Ethylene bromide	A 4
Ethylene chloride	A 3
Ethylene chlorohydrin	A 5
Ethylene dibromide	A 4
Ethylene dichloride	A 3
Ethyl fluid	M 2
Ethyl plumban	M 2

F

Fibrous serpentine P 1
Fluoride of potassium P 4
Fluoride of sodium P 4
Fluorides P 4
Fluorite P 4
Fluorol P 4
Fluor spar P 4
Fluosilicic acid L 8
Formaldehyde N 1
Formalin N 1
Formic aldehyde N 1
Formol N 1
Formyl hydrate N 1
2,4-Furandione L 1

G

Glucina M 4
Glucinium M 4
Glycol chlorohydrin A 5

H

Hornblende asbestos P 1
Horn lead M 2
Hydrated chromium(III)oxide M 6
Hydrochloric acid L 3
Hydrocyanic acid E 1
Hydrofluoric acid gas L 2
Hydrofluoride of potassium P 4
Hydro-fluosilicic acid L 8
Hydrogen chloride L 3
Hydrogen cyanide E 1
Hydrogen fluoride L 2
Hydro-silicofluoric acid L 8
Hydroxybenzene G 1
Hydroxytoluene G 2

K

King's yellow	M 6
Kremnitz white	M 2

L

Lead	M 2
Lead (II) acetate	M 2
Lead (II) carbonate	M 2
Lead (II) chloride	M 2
Lead chromate (VI)	M 6
Lead monoxide	M 2
Lead (II) nitrate	M 2
Lead (II) orthoplumbate (IV)	M 2
Lead (II) oxide	M 2
Lead (II, IV) oxide	M 2
Lead spar	M 2
Lead (II) sulphate	M 2
Lead tetraethyl	M 2
Lead tetramethyl	M 2
Lead vitriol	M 2
Leipzig yellow	M 6
Litharge	M 2
Lithargite (red)	M 2
Lupranat T80	C 1

M

Maleic anhydride	L 1
Massiot (yellow)	M 2
Mercuric nitrate	M 1
MDI	C 2
Mercury	M 1
Mercuric chloride	M 1
Mercury (II) chloride	M 1
Mercury (II) nitrate	M 1
Mercury (II) sulphate	M 1
Methyl aldehyde	N 1

Methylbenzene H 3
Methyl chloride A 7
Methylchloroform A 2
Methylphenol G 2
Methyl plumban M 2
Minium M 2
Mountain flax P 1
Muriatic acid L 3

N

Naphtha K 1
New yellow M 6
Nitrate of lead M 2
Nitric acid L 6
Nitrobenzene B 3
Nitrobenzol B 3
p-Nitrochlorobenzene B 4
Nitromethylbenzene B 2
Nitrotoluene B 2

O

Oil of mirbane B 3
Oil of vitriol L 7
Oxalic acid L10
Oxybenzene G 1

P

Paris yellow M 6
Pattinson's white lead M 2
Penta G 4
Pentachlorophenol G 4
Phenol G 1
Phenylamine B 1
Phenyl ethylene O 1
Phenyl hydroxide G 1
Phenylmethane H 3

Phosgene P 3
Phthalandione L 11
Phthacic anhydride L 11
Potash lye L 4
Potassium bichromate M 6
Potassium bifluoride P 4
Potassium chromate (VI) M 6
Potassium cyanide E 3
Potassium dichromate (VI) M 6
Potassium fluoride P 4
Potassium hydrate L 4
Potassium hydrogen fluoride P 4
Potassium hydroxide L 4
Propenal N 2
Propenenitrile D 1
Propylene chloride A 11

Q

Quinone G 3
p-Quinone G 3

R

Red lead M 2
Red lead oxide M 2
Red oxide of lead M 2

S

Selenium M 7
Silicofluoric acid L 8
Soda lye L 5
Sodium bichromate M 6
Sodium bifluoride P 4
Sodium chromate (VI) M 6
Sodium cyanide E 2
Sodium dichromate (VI) dihydrate M 6
Sodium fluoride P 4
Sodium hydrate L 5

Sodium hydrogen bifluoride P 4
Sodium hydroxide L 5
Stibine M 5
Styrene O 1
Sugar of lead M 2
Sulphuric acid L 7

T

Tar oil K 1
Tetraethyllead M 2
Tetraethyl plumban M 2
Tetramethyllead M 2
Tetramethyl plumban M 2
Toluene H 3
Toluene diisocyanate (TDI) C 1
Toluol H 3
Tolylene diisocyanate C 1
Trichloroethane A 2
1,1,1-Trichloroethane A 2

V

Valentinite M 5
Villiaumite P 4
Vinyl benzene O 1
Vinyl cyanide D 1

W

White antimony M 5
White lead M 2
White lead ore M 2

X

Xylene H 1
Xylol H 1

Z

Zinc chromate(VI) M 6
Zinc yellow M 6